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**Sulfate soap separation and acidulation
Part 2. Composition of the soaps
KCL Reports 2874**

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SULFATE SOAP SEPARATION AND ACIDULATION

Part 2. Composition of the soaps

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SULFATE SOAP SEPARATION AND ACIDULATION

Part 2. Composition of the soaps

EXECUTIVE SUMMARY

Nearly 60 soap samples were collected from all the Finnish kraft pulp mills and analyzed for tall oil and for various impurities. The results thus reveal the current ranges in the amounts of the impurities in the domestic soaps, which can also be used as an indication for the lowest reasonable figures. Special attention was now paid to the isolation and detailed characterization of fibers and other solid impurities. The nature of this fraction varied a lot, being only partly dependant on the cooking conditions and soap separation and handling systems.

Value to the customers

Different impurities in the sulfate soaps can restrict soap separation, lowering its recovery from black liquors. They can also reduce soap quality, resulting in increased acid consumption during acidulation and in reduced recovery of crude tall oil. All these factors also mean that more soap or tall oil is sent to black liquor evaporation where they may cause additional problems. Detailed information on the soap impurities and factors affecting them is therefore essential for planning process improvements. In this study, a comprehensive sampling and analysis campaign was conducted for comparison of Finnish sulfate soaps

Technical objectives

The main objective of the present study was to determine the effect of different solid impurities on the soap separation and soap quality problems. Means to overcome the problems were also to be suggested. The objective was approached by analyzing not only the final soaps (acidulation feeds) from all the Finnish mills, but also soap samples from different soap separation points.

The main results: impurities, their natures and concentration ranges

The collected soap samples were analyzed for the content and composition of tall oil, and for various organic and inorganic impurities. Specific attention was paid to the isolation and characterization of fibers and other solid impurities. Altogether, the analyses indicated that:

- The soap compositions may vary for many different reasons, such as the pulping raw materials, cooking conditions, and other factors affecting the composition of black liquors, and applied soap separation and handling (washing) systems.
- Typically, the tall oil content varied from 50 to 60%. Its composition was affected by the pulping raw material. Varying amounts of tall oil are lost during acidulation, due to the interactions with the lignin phase.
- The fibers and other solid impurities were isolated after hydrochloric or sulfuric acid acidulation, and studied under microscope. The typical fiber amounts were 1-5 g/kg

which is clearly less than frequently reported. The relatively low current amounts may be a result of careful washing of the isolated materials with acetone, to dissolve tall oil residues. It was also found necessary to wash the residues from sulfuric acid acidulation to dissolve crystals of sodium sulfate.

- The nature of the fiber fractions could vary dramatically, from clean fiber nets to a mess of fibers in a matrix of resin-type material, defoamers and other, poorly characterized constituents.
- The correlations between the cooking conditions, amount of the fibers and their nature were not straightforward.
- The amount of turpentine in the soaps varied from 0.1 to 20 g/kg. The highest amounts were usually found in the soaps from weak liquor tanks of the softwood mills.
- The amount of lignin typically varied from 5 to 10 g/kg.
- The amount of hydroxy acids and other polar compounds were c. 10-15 g/kg. They represent typical black liquor compounds, and no relative enrichment of potential calcium scavengers (such as oxalic acid) could be detected.
- Silicone-based defoamers could not be directly detected in the soaps, but their occasional presence in the isolated fiber fractions was evident. Their role as soap impurities remain, however, poorly characterized.
- Calcium was the most abundant of eight analyzed non-process elements, typically ranging from 1 to 3 g/kg (occasionally up to 6.5 g/kg). Indirect evidence was gathered to rule out carbonate and oxalate as calcium scavengers, suggesting that most of it should be bound to fatty and resin acids.
- Other main non-process elements in the soaps were silicon and magnesium, up to 0.7 and 1.8 g/kg, respectively.
- Laser ablation (evaporation) studies on the distribution of the non-process elements in the soaps typically revealed nearly identical distribution patterns for aluminum, zinc and phosphorus. This suggests that phosphate forms insoluble salts for many metallic non-process elements.

Exploitation of the results

The current results clearly demonstrate that the composition of the sulfate soaps may vary a lot, although the typical ranges for many compounds or fractions may be relatively narrow. There are apparently many reasons for the variations, such as the pulping raw materials, cooking conditions, and other factors affecting the composition of black liquors, and applied soap separation and handling (washing) systems. This will make it a challenging task to link certain impurities to certain process conditions, operational parameters or other factors. Some links are, however, more evident.

Altogether, the current work covers analytical results for 58 soap samples from all the Finnish kraft pulp mills. The soaps include both the final acidulation feeds, and whenever possible, also selected samples from different soap separation or handling points. This forms a comprehensive overview of the domestic soaps, apparently also giving some guidelines on the lowest possible impurity contents that can be reached.

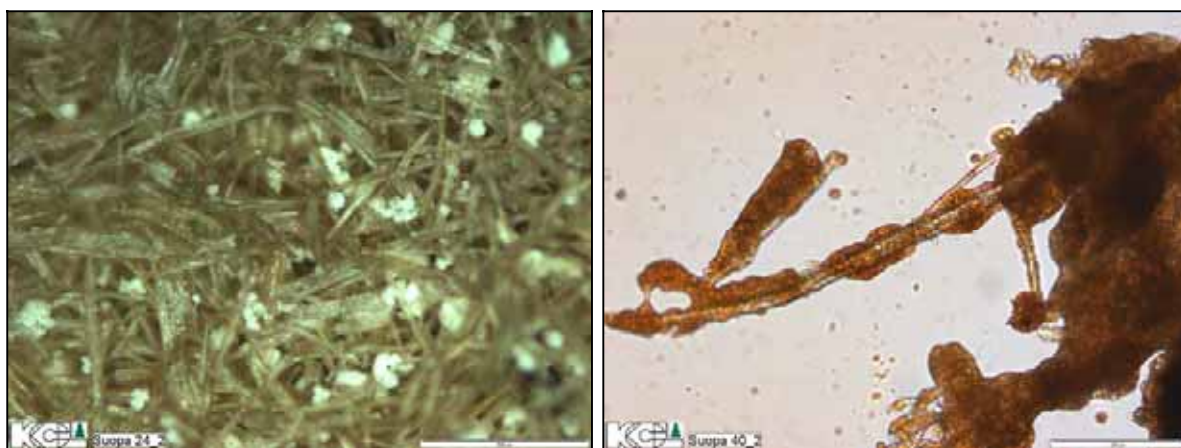
Fibers in soaps – a controversial matter

Although it is well-known that all the soaps contain some fibers and other solid impurities ("dirt"), their role in the soap separation and quality problems is still under discussions. It looks that little attention has so far been paid to more detailed characterization of this fraction.

Detailed studies of numerous fiber fractions indicated that they can vary a lot, from clean fibers to different messy matrices, with varying amounts of fibers in them (Figs. 1–4). It also became evident, through careful washing procedures, that the amount of fibers is typically much lower than usually reported. In this study, the typical content of the fibers was from 1-5 g/kg. It also became apparent that the cooking conditions have only marginal effect on the fiber contents in the soaps.



Figs. 1–2. Examples of clean and dirty fiber fractions isolated from sulfate soaps. The dark *separate* spots may represent defoamers, lignin, or resin-type-material.



Figs. 3–4. Further examples on the nature of the isolated fiber fractions. A fiber mat (left) with some remaining calcium sulfate crystals, and fibers covered by some defoamer-resin-type material (right).

The other material isolated (in varying amounts) with the fibers could be only partially characterized. Evidently, there may be iron (rust) and other inorganic salts, as well as defoamers, lignin, and occasionally resin-type material. Part of that may be unacidulated fatty and resin acids.

Other organic impurities – lignin is important

Other analyzed organic impurities included turpentine, lignin, defoamers, and hydroxy acids. Of them, defoamers and hydroxy acids have not been previously analyzed in the soaps. Any defoamers could be only occasionally detected, but the hydroxy acids were found in each analyzed soap sample. However, no enriched amounts of any known calcium-complexing hydroxy acids were found.

The amounts of lignin were typically quite low (less than 10 g/kg), but even this can cause problems for the recovery of crude tall oil after soap acidulation. Sufficient washing (decanting) increases lignin removal. The role of turpentine in soap separation is not fully known; its amounts now varied from 0.1 to 20 g/kg.

Non-process elements

In all, eight different non-process elements were analyzed from all the collected soap samples. In addition, a novel analytical method – based on laser ablation (vaporization) of the elements from frozen soap surfaces – was used to study their relative distribution. This way, it could be monitored which type of compounds they form. According to the results, zinc and aluminum occur as insoluble phosphates, but magnesium is not typically in the form of magnesium silicate.

In each case, the main non-process element was, however, calcium. Its content was occasionally as high as 6.5 g/kg, although it typically ranged from 1 to 3 g/kg. No evidence for the presence of calcium carbonate was found.

Other reports and publications of the project

Niemelä, K. Sulphate soap separation and acidulation. Literature review on process improvements. KCL Reports 2720 (STFI report CHEM 96), 2003, 50 p.

Sirén, K. Calcium carbonate scaling in black liquor evaporation. KCL Reports 2824 (2006), 105 p.

Sirén, K. Mechanisms and rate of soap separation. KCL Reports 2875 (2007), 64 p.

Pajula, E. and Sirén, K. Calcium carbonate scaling in black liquor evaporation. Part 2: Multivariate analysis of mill data. KCL Reports 2876 (2007), 38 p.

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Sirén, K. Calcium carbonate scaling in black liquor evaporation. International Chemical Recovery Conference, Quebec City, Canada, May 29 – June 1, 2007, p. 485–488.

SULFATE SOAP SEPARATION AND ACIDULATION

Part 2. Composition of the soaps

EXECUTIVE SUMMARY

Kaikilta Suomen sellutehtailta kerättiin yhteensä lähes 60 suopanäytettä, joiden koostumukset analysoitiin (erityisesti erilaiset epäpuhtaudet). Aineiston perusteella selvitettiin eri epäpuhtauksien nykyiset vaihtelurajat samoin kuin niiden alhaisimmat saavutettavissa olevat tasot. Työssä kiinnitettiin erityistä huomiota suovan sisältämiin kuituihin ja muihin kiinteisiin epäpuhtauksiin. Niissä todettiin runsaasti eroja eri tehtaiden välillä, mitä voidaan vain osittain selittää keitto-olosuhteiden ja suovan eri käsittelytapojen avulla.

Tutkimuksen arvo asiakkaalle

Suovan sisältämät erilaiset epäpuhtaudet voivat heikentää sen erottumista mustalipeästä vähentäen suovan ja mäntyöljyn saantoa. Epäpuhtaudet voivat myös heikentää suovan laatua mikä saattaa esimerkiksi lisätä rikkihapon kulutusta mäntyöljyn keitossa. Tämä voi johtaa siihen että huomattava osa suovasta tai mäntyöljystä palautuu emäveden mukana takaisin kemikaalikiertoon, jossa saattaa syntyä erinäisiä lisäongelmia. Yksityiskohtaiset tiedot suovan eri epäpuhtauksista ja niihin vaikuttavista tekijöistä ovat sen vuoksi oleellisia mahdollisten prosessimuutosten pohjaksi. Tässä työssä kerättiin ja tutkittiin kattava erä kotimaisten sulfaattitehtaiden suopanäytteitä.

Tekniset tavoitteet

Työn keskeisin tavoite oli selvittää suovan erilaisten kiinteiden epäpuhtauksien vaikutukset suovan erottumiseen ja laatuun, pyrkimyksenä myös ehdottaa ratkaisuja vastaaviin ongelmiin. Tavoitetta lähestyttiin analysoimalla suuri joukko suopanäytteitä kaikilta kotimaisilta sellutehtailta; mukana oli sekä mäntyöljynkeittoon menevät (lopulliset) suovat että eri suovanerotusvaiheista kerätyt näytteet.

Päätulokset: eri epäpuhtaudet, niiden koostumukset ja vaihteluvälit

Kerätyistä suopanäytteistä analysoitiin mäntyöljyn pitoisuus ja sen koostumus sekä joukko orgaanisia ja epäorgaanisia epäpuhtauksia. Erityistä huomiota laitettiin kuitujen ja muiden kiinteiden epäpuhtauksien eristämiseen ja karakterisointiin. Saatujen tulosten mukaan:

- Suovan koostumukset voivat vaihdella hyvin monien eri tekijöiden vaikutuksesta; tällaisia tekijöitä ovat mm. keiton raaka-aine, keitto-olosuhteet, ja monet muut tekijät jotka vaikuttavat mustalipeän koostumukseen, sekä käytetyt suovan erotus- ja käsittelytavat.
- Suovat sisältävät mäntyöljyä tyypillisesti 50–60 %. Mäntyöljyn koostumus puolestaan riippuu keiton raaka-aineesta. Mäntyöljykeiton yhteydessä menetetään emäveden ligniinifaasin mukana vaihtelevia määriä mäntyöljyä.
- Kuidut ja muut kiinteät epäpuhtaudet eristettiin suolahappo- tai rikkihappokeiton jälkeen, ja niitä karakterisoitiin mikroskoopin avulla. Tyypillisesti kuituja ja muita

kiintoaineita todettiin suovassa 1–5 g/kg mikä on selvästi vähemmän kuin useimmin kirjallisuudessa raportoidut arvot. Nyt todettuihin suhteellisen alhaisiin arvoihin saattavat vaikuttaa käytetyt erotusmenetelmät: suodatuksen yhteydessä erottuneita kiintoaineita pestiin asetonilla mäntyöljyjäämien poistamiseksi. Lisäksi todettiin, että rikkihappokeiton jälkeen erotettuja kiintoainekerääntymiä on pestävä suolahapolla, muodostuneiden kalsiumsulfaattikiteiden liuottamiseksi.

- Eri suopanäytteistä eristetyt kuitufraktiot saattoivat vaihdella todella huomattavasti, puhtaista kuitumatoista erinäisten hartsimaisten aineiden, vaahdonestoaineiden, tai vaatimattomasti karakterisoitujen materiaalien peittämiin kuitumössöihin.
- Selkeitä korrelaatioita ei voitu osoittaa keitto-olosuhteiden ja suovan sisältämien kuitujen määrän tai luonteen välillä.
- Suopien sisältämän tärpätin määrä vaihteli välillä 0,1–20 g/kg. Suurimmat tärpättipitoisuudet löydettiin tavallisesti heikkolipeäsäiliöissä erotetuista havukeiton suovista.
- Ligniinin määrä suopanäytteissä vaihteli tavallisesti välillä 5–10 g/kg.
- Hydroksihappojen ja muiden polaaristen yhdisteiden pitoisuudet suopanäytteissä olivat tasolla 10–15 g/kg. Kaikki todetut yhdisteet edustavat tyypillisiä mustalipeä-yhdisteitä. Näiden suhteelliset pitoisuudet vastasivat niiden pitoisuuksia mustalipeässä, eikä minkään tunnetun kalsiumia sitovan yhdisteen (kuten oksaalihapon) voitu osoittaa rikastuneen suopaan.
- Silikonipohjaisia vaahdonestoaineita ei voitu varmuudella osoittaa suoraan suovasta, mutta ajoittain niitä löydettiin eristetyistä kuitufraktioista. Vaahdonestoaineiden todellinen merkitys suovan mahdollisena epäpuhtautena jäi kuitenkin huonosti todennettua.
- Kalsium oli runsain kaikista kahdeksasta nyt analysoidusta vierasaineesta (alkuaineesta), sen pitoisuuden tyypillisesti vaihdellessa alueella 1–3 g/kg (enimmillään kuitenkin yli 6 g/kg). Suurin osa kalsiumista on todennäköisesti sitoutunut rasva- ja hartsihappoihin, sillä esim. kalsiumoksalaatin ja kalsiumkarbonaatin mahdollisuudet voitiin epäsuorasti sulkea pois.
- Muita keskeisiä suovan vierasaineita olivat pii ja magnesium, joiden todetut maksimipitoisuudet olivat 0,7 ja 1,8 g/kg.
- Vierasaineiden keskenään muodastamia yhdisteitä pyrittiin suopanäytteistä jäljittämään laserhöyrystyksen avulla, jolloin voitiin seurata niiden pitoisuusvaihtelujen samankaltaisuuksia. Useissa tapauksissa todettiin lähes identtiset jakaumakäyrät alumiinille, sinkille, ja fosforille. Tästä voidaan päätellä alumiini- ja sinkkifosfaattien esiintyminen suovassa.

Tulosten hyödyntäminen

Saadut analyysitulokset osoittavat eri tehtailta ja eri vaiheista kerättyjen suopanäytteiden voivan vaihdella melkoisestikin, vaikka monien yhdisteiden tai fraktioiden tyypilliset vaihteluvälit saattoivat olla varsin kapeat. Todettuihin vaihteluihin vaikuttavat ilmeisesti useat eri tekijät, kuten keiton raaka-aine, keitto-olosuhteet, muut mustalipeän koostumukseen vaikuttavat tekijät, ja käytössä olevat suovan erotus- ja käsittelytekniikat. Tämän vuoksi on varsin haastavaa pyrkiä löytämään selkeitä yhtäläisyyksiä suovan sisältämien epäpuhtauksien ja käytettyjen prosessiolosuhteiden tai muiden tekijöiden välille. Eräitä tällaisia yhtäläisyyksiä voidaan kuitenkin todeta.

Tässä työssä analysoitiin vaihtelevalla tarkkuudella kaikkiaan 58 suopanäytettä, jotka edustivat kaikkia kotimaisia sellutehtaita. Näytteiden joukossa oli lopulliset, mänty-öljykeittoon menevät suovat, samoin kuin mahdollisuuksien mukaan eri suovanerotusvaiheista kerätyt näytteet. Laajan kattavuuden ansiosta voidaan tuloksia nyt käyttää myös alhaisimpien saavutettavissa olevien epäpuhtaustasojen arviointiin.

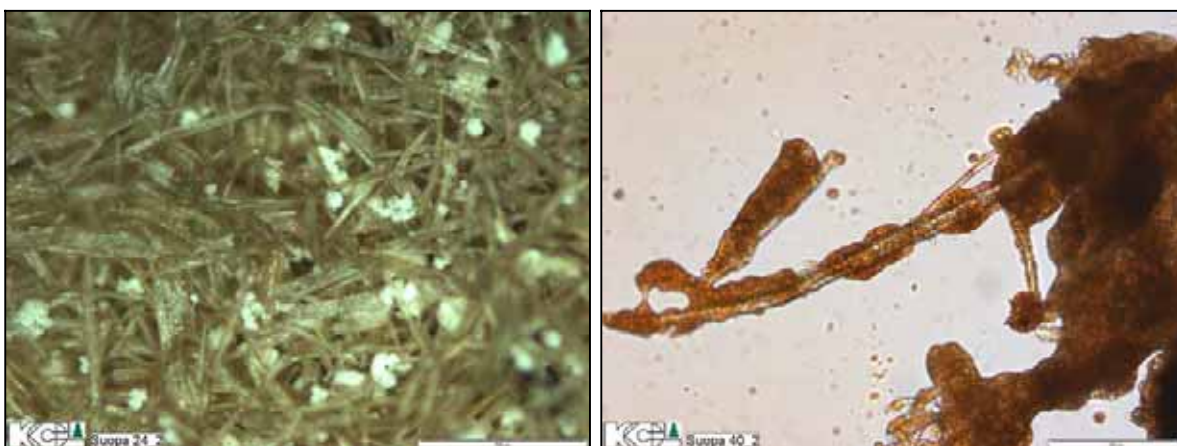
Suovan kuidut – riidanalainen kysymys

Kaikki suovat sisältävät tunnetusti ainakin jonkin verran kuituja ja muita kiinteitä epäpuhtauksia ("likaa"), mutta yksimielisiä ei olla niiden merkityksestä suovan laatu- ja erotusongelmissa. Vaikuttaa siltä, että varsin vähäistä huomiota on toistaiseksi kiinnitetty kuitujen ja muiden kiintoaineiden yksityiskohtaisempaan karakterisointiin.

Nyt toteutetut yksityiskohtaiset tutkimukset osoittivat, että suovasta eristetyt kuidut ja muut kiintoaineet voivat vaihdella huomattavasti, puhtaista kuitumatoista aina erilaisiin kuituja sisältäviin seoksiin (kuvat 1–4). Eristettyjen kiintoainefraktioiden huolellisilla pesuilla päästiin aikaisempaa selvästi alhaisempiin kiintoainepitoisuuksiin (tyypillisesti 1–5 g/kg). Lisäksi osoittautui, että eri keittomenetelmillä on ilmeisesti vain vähäinen vaikutus suovan kuitupitoisuuksiin.



Kuvat 1–2. Esimerkkejä suovasta eristetyistä puhtaista ja likaisista kuiduista. Erilliset tummat partikkelit (oik.) saattavat sisältää mm. ligniiniä, keittymätöntä suopaa tai vaahdonestoaineita.



Kuvat 3–4. Lisäesimerkkejä suovasta eristetyistä kuiduista. Vas. kuitumaton sisään jäänyttä kalsiumsulfaattia, ja oik. vaahdonestoaineen tai uuteaineiden peittämiä kuituja.

Kuitujen mukana eristetty muu materiaali (esim. kuvat 2 ja 4) saatiin vain osittain karakterisoitua. Selvää kuitenkin on, että läsnä saattaa olla rautaa (ruostetta), erilaisia epäorgaanisia suoloja, vaahdonestoainetta, ligniiniä, ja ajoittain hartsimaista tai uuteainetyyppistä materiaalia (lehtipuun neutraaliuuteainekasaumia tai keittymätöntä suopaa).

Muut orgaaniset epäpuhtaudet – ligniinillä suuri merkitys

Muut tutkitut orgaaniset epäpuhtaudet olivat tärpähti, ligniini, vaahdonestoaineet ja hydroksihapot. Näistä vaahdonestoaineita ja hydroksihappoja ei tiettävästi ole aikaisemmin analysoitu suovista. Nyt hydroksihappoja löydettiin kaikista tutkituista suovista, mutta vaahdonestoaineita vain ajoittain. Kalsiumia tunnetusti kompleksoivien hydroksihappojen minkäänlaista rikastumista (muihin mustalipeän hydroksihappoihin nähden) ei kuitenkaan todettu.

Ligniinin pitoisuudet olivat tyypillisesti varsin alhaisia (alle 10 g/kg), mutta kuitenkin riittäviä aiheuttamaan ongelmia mäntyöljyn erotuksessa keiton jälkeen. Tunnetusti riittävä suovan pesu (dekantointi) vähentää ligniinin määrää. Tärpätin merkitys suovan erotuksen yhteydessä on huonommin tunnettu; nyt sen pitoisuudet vaihtelivat välillä 0,1–20 g/kg.

Vierasaineet

Kaikista suopanäytteistä analysoitiin kahdeksan eri vierasainetta (alkuainetta). Lisäksi käytettiin laserhöyrystykseen perustuvaa uutta menetelmää vierasainejakaumien tutkimiseen, tarkoituksena selvittää mitkä niistä voivat muodostaa keskenään yhdisteitä. Todettujen jakaumien perusteella on esimerkiksi syytä uskoa että alumiini ja sinkki esiintyvät fosfaatteina, mutta magnesium ei juurikaan esiinny magnesiumsilikaattina.

Poikkeuksetta kalsium oli hallitseva vierasaine kaikissa suopanäytteissä. Sen pitoisuus oli enimmillään yli 6 g/kg, vaikkapa tavanomaisin pitoisuusalue oli 1–3 g/kg. Kalsium-karbonaattia ei suovasta pystytty osoittamaan.

Projektin muut raportit

Niemelä, K. Sulphate soap separation and acidulation. Literature review on process improvements. KCL Reports 2720 (STFI report CHEM 96), 2003, 50 s.

Sirén, K. Calcium carbonate scaling in black liquor evaporation. KCL Reports 2824 (2006), 105 s.

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Sirén, K. Calcium carbonate scaling in black liquor evaporation. International Chemical Recovery Conference, Quebec City, Canada, May 29 – June 1, 2007, s. 485–488.

1 INTRODUCTION

Background. – Studies on the separation and properties of sulfate soap were commenced at KCL in September 2003, as a part of the project *Extractives* in KCL-STFI chemical pulp joint research program. The joint program was planned for 2003–2005 (Axegård and Poppius-Levlin 2003), but it was unexpectedly terminated after the first year. During 2003, a literature review was compiled (Niemelä 2003) but no experimental work was yet performed. The main purpose of the review work was to assist in more detailed planning of experimental work, by summarizing the current knowledge in selected areas and by pointing out those that should require the most urgent attention. The work was focused on the following main questions: soap separation and factors affecting it, soap quality, and soap acidulation.

The experimental work on the soap separation was commenced in 2004, now as a part of the project *Calcium carbonate scaling and soap separation*, formed from two separate sub-projects in the KCL-STFI research program. The results from the first phase of the experimental work are presented and discussed in the current report. The planning of these experiments was mainly based on the outcome of the review (Niemelä 2003) and on the results of recent mill-scale investigations on the soap separation and quality (Räsänen 2003). It became evident that deeper information is required on various solid impurities in soap, on their origins and on their effects on soap separation and quality.

Objectives. – The main objective of the present study was to determine the effect of different solid impurities on the soap separation and quality problems. Means to overcome the problems were also to be suggested.

Approaches. – The main approach to achieve the objectives was to collect the soap samples from all the Finnish kraft pulp mills and to subject them to detailed analyses for their composition, particularly for the impurities. In all, nearly 60 soap samples were thus collected for the investigations. These naturally included the samples of soap feeding the acidulation reactors, but whenever possible, soap samples from different separation stages were also collected.

The analytical work was supported by the survey of the process data on the separation and handling of the soaps at the mills. This was used to search for possible correlations between the soap composition (impurities) and the process conditions. It should be noted, however, that no analyses of the corresponding black liquors were now conducted.

Identification of the mills. – As will be seen, the mills are fully identified with each soap sample in this report. This was agreed by all the participating mills, just to eliminate any inevitable speculation between the samples, released process conditions and the mills. This was also taken into consideration by double-checking that no confidential information is accidentally revealed on the process conditions and other mill-specific details.

2 EXPERIMENTAL

As briefly mentioned in the Introduction, the work was composed of the analysis of the soap samples from all the Finnish mills, and of the comparison of these results with the process data. The data on the process conditions and certain other factors was collected by a questionnaire sent to the mills, as described in more detail in Section 2.1.

The collected soap samples are listed and briefly commented on in Section 2.2. The conducted analytical determinations can be classified into two main groups. The first group of the analyses are those that could be performed for the soap samples as received, i.e. without preceding acidulation. These analyses are described in Section 2.3. A number of other determinations (Section 2.4) required the preceding acidulation which was conducted by hydrochloric or sulfuric acid.

2.1 Survey of the process conditions

The survey for all the kraft pulp mills was conducted in April–May 2004, with the aim to collect data on the process conditions and other factors related to the 1) use of additives in the fiber lines, 2) separation and handling of the soap, and 3) acidulation of the soap. The questions covered by the survey are briefly listed below.

1. The use of defoamers and other additives

- The types and amounts of the additives used in the fiber lines (in order to identify the additives that could also be found in the soaps as impurities).

2. The separation and handling of the soap

- Total amount of the recovered soap.
- Distribution of the soap recovery between wash liquor, feed liquor, and intermediate liquor tanks.
- Soap separation methods.
- Soap handling (washing) before acidulation.

3. The acidulation of the soap

- Acidulation process and chemicals.
- Yield of tall oil.
- Production figure of tall oil.
- Returning point of tall oil acidulation spent acid to the recovery system.

In addition, the mills were asked to specify their own research needs on soap separation and handling (if any). All the mills responded to the survey.

The results of the survey are briefly presented in the Appendix 6. The presentation and discussion of the analytical results for the soaps (in Chapter 3) requires some comparison with the data compiled in the Appendix 6.

2.2 Collected soap samples

In all, 58 samples were collected at 17 mills, representing 1–6 soap samples per mill (Table 1). Whenever possible, soap samples were withdrawn from different liquor tanks. Most of the samples were collected by the mill staff.

Table 1. Collected soap samples.

Mill*	Collected soap samples
Botnia, Joutseno	Weak/feed liquor, intermediate liquor, acidulation feed
Botnia, Kaskinen	Feed liquor, intermediate liquor, acidulation feed (birch), acidulation feed (aspen campaign)
Botnia, Kemi	Feed liquor, collection tank, acidulation feed
Botnia, Rauma	Collection tank, acidulation feed
Botnia, Äänekoski	Acidulation feed
Sunila	Collection tanks 1 and 2, handling tanks 1 and 2, acidulation feed
Stora Enso, Enocell	Feed liquor (2), intermediate liquor, acidulation feed
Stora Enso, Imatra	Storage tanks (2), acidulation feed (2)
Stora Enso, Kemijärvi	Wash liquor, feed liquor, intermediate liquor, acidulation feed
Stora Enso, Kotka	Feed liquor, intermediate liquor, acidulation
Stora Enso, Oulu	Acidulation feed
Stora Enso, Varkaus	Weak liquor (2), intermediate liquor, acidulation feed
Stora Enso, Veitsiluoto	Wash liquor, feed liquor (2), intermediate liquor (2), acidulation feed
UPM, Kaukas	Evaporation/chemical plant, acidulation feed
UPM, Kymi	Feed liquor (2), intermediate liquor (2), acidulation feed
UPM, Pietarsaari	Collection tank, storage tank, acidulation feed
UPM, Tervasaari	SAP soap, kraft weak liquor, kraft intermediate liquor, acidulation feed

*Hereafter, only the mill names (not companies) are used in the text.

Due to the high number of the soap samples, it was not reasonable to subject each of them to the same detailed analytical procedures. Therefore, the main focus was now in the soap materials entering the acidulation reactors. In addition, a representative amount of other soap samples were analyzed in less detail for various specific questions. This way, for example, it was possible to monitor certain changes that take place in the soap composition as a function of liquor processing, i.e. by comparing soaps separated in the feed and intermediate liquor tanks.

As described in the Sections 2.3 and 2.4, a number of analytical procedures were applied for the soap samples. Many of them can be regarded as routine methods and will not be described in detail. In addition, a number of novel methods were also tested and applied. Some of them required a certain amount of development work.

2.3 Analyses of the soaps without acidulation

The soaps were analyzed *as received* for:

- dry matter contents
- sodium and potassium
- main non-process elements (NPEs): Ca, Mg, Si, Fe, Al, P, Mn, Zn
- distribution of sodium, potassium, and certain non-process elements
- turpentine (and other volatile neutral compounds)
- silicone (defoamers)

Dry matter contents and elements. – All the soap samples were analyzed for the dry matter contents (SCAN-N 22) and different elements, using either flame atomic absorption mass spectrometry (Na and K) or inductively coupled plasma atomic emission spectroscopy (ICP-AES, other elements). Brief description of these methods has been given by Sirén (1998). The choice of the main non-process elements was based on the previous studies on soap impurities, as conducted at KCL (e.g. Järvinen 1996) and elsewhere (cf. Section 3.2).

Distribution of the elements. – The distribution of various elements was investigated for 19 soap samples. In the applied method, small amounts of soap were frozen (–80 °C) and subjected to laser ablation (LA) to vaporize surface elements. The elements of interest were then analyzed by ICP-MS (inductively coupled plasma mass spectrometry). This way, it was possible to follow the distribution patterns of various elements and to study which of them most likely form chemical compounds together.

The LA ICP-MS studies were conducted at Åbo Akademi University, in the Laboratory of Analytical Chemistry. The equipment and method details have been given by Ek (1998) and Su (2004) who have studied distribution of different metals in single pulp fibers. In the current measurements, speed of laser beam on the soap surface was 50 µm/s and typical analysis time for one run was 3 min. Before freezing and analysis, the soap samples were pressed between two teflon plates to get smooth surfaces.

Attempts were also conducted at KCL to determine the distribution patterns of the main non-process elements by EDX. It turned out, however, that their concentrations were not high enough for successful distribution mapping.

Turpentine. – Two different approaches were used for the analysis of turpentine and other volatile compounds: gas chromatography – mass spectrometry (GC–MS) after solvent extraction, and quantitative head-space GC. In the first method, soap samples of varying sizes were first extracted with ether or hexane. The preliminary experiments indicated that hexane is a more suitable solvent and that 500 mg is a suitable soap mass; these were adopted for further studies. The extracts could then be analyzed as such (i.e. without any concentration) by GC–MS for the *identification* of the turpentine compounds and other neutrals, as described by Niemelä (2000, 2001). This also allowed a rapid profiling of the turpentine in the soaps, as will be discussed in Section 3.X. The interpretation of the mass spectra was based on the use of a commercial library and other spectral collections available at KCL (Niemelä 2000, 2001).

As the first GC–MS analyses revealed the presence of several neutral diterpenes and other less-volatile compounds, attempts were made to increase the detection of diterpene and triterpene alcohols and related compounds. For this purpose, selected ether and hexane extracts were evaporated to dryness and the evaporation residues were trimethylsilylated before the GC–MS analyses.

After the GC–MS profiling of the hexane extracts, the main turpentine compounds were quantified in the selected soap samples by head-space GC. The analysis was conducted by an HP 5890 gas chromatograph, equipped with an HP-FFAP capillary column (25 m × 0.32 mm i.d., phase thickness 0.52 µm). The other operation conditions were:

- splitless injection, injector temperature 150 °C
- temperature program 60 °C for 9 min, 20 °C/min → 240 °C (2 min)
- flame-ionization detector, temperature 280 °C
- static head-space injector Tekmar 7000, equilibrium time 23 min at 60 °C
- calibration by the internal standard (toluene) method, including correction for methanol present in the soap samples

Silicone defoamers. – The possible presence of any traces of the silicone defoamers in the soaps was approached by two separate methods: LA ICP-MS after spiking the soaps with defoamers, and hexane extraction followed by FTIR. For these investigations, five soap samples (with highest silicon contents) were used.

For the LA ICP-MS determinations, the selected soap samples were spiked with the defoamers used in the corresponding mills, to roughly double the silicon contents. It was expected that the silicon distribution curves would increase in case the original silicon is derived from the defoamers.

In the second approach, five soap samples were extracted with acetone, the extracts were concentrated and the concentrates analyzed by FTIR (cf. Auterinen 2000).

2.4 Analyses of the soaps via acidulation

The rest of the analyses required the preceding acidulation of the soap samples. This approach was used to determine:

- composition of crude tall oil (separated spontaneously after acidulation)
- amount and composition of the total tall oil
- lignin
- hydroxy acids and other hydrophilic compounds
- fibers and other solid impurities

For the acidulations, both hydrochloric and sulfuric acids were applied. As described later in more detail, it was necessary to conduct three main sets of acidulations:

- Acidulation of 50-g soap samples with 4 M hydrochloric acid.
- Acidulation of 150-g soap samples with 4 M hydrochloric acid.
- Acidulation of 150-g soap samples with 2 M sulfuric acid.

The 50-g soap samples were used for the analysis of tall oil (total oil and spontaneously separated), lignin, and hydroxy acids. The higher soap quantities (150 g) were required for the successful isolation and characterization of fibers and other solid impurities.

50-g soap samples, acidulation and analysis. – In all, 22 soap samples of 50 g were acidulated under stirring with 100 ml of 4 M hydrochloric acid, at 80–85 °C for 2 h. The main reason for the use of hydrochloric acid was the planned analysis of the hydroxy acids from the resulting spent acids – this would be much more tedious and problematic in the presence of high amounts of sulfate.

After the acidulation, the following analyses were conducted for different fractions:

- A small sample (< 50 mg) of the separated oil was taken for the GC–MS analysis of its composition (after derivatization by trimethylsilylation).
- The acidulation mixtures were transferred into the separatory funnels and extracted twice with c. 150 ml of ether, to isolate the total tall oils. The ether phases were recovered, combined, and evaporated to dryness. The amount of the isolated oil was determined, and its composition analyzed by GC–MS.
- The aqueous phase (spent acid) was recovered from the separatory funnels, and 3-ml samples were taken for the analysis of hydroxy acids and other polar compounds. The applied procedure involved addition of xylitol (0.5 mg) as the internal standard, cation-exchange to H⁺ form, evaporation to dryness, trimethylsilylation, and GC–MS analysis (Alén et al. 1984, Niemelä and Sjöström 1986).
- Finally, the lignin fraction was recovered from the separatory funnels and dissolved in 1 M NaOH solution (the funnels were also washed with the NaOH solution). Content of lignin in the combined NaOH solutions were determined by UV.

The 22 soap samples analyzed in the above way can be identified in Appendices 1a and 1c on the basis of the reported total tall oil contents.

150-g soap samples, acidulation and analysis. – In all, 16 and 26 soap samples of 150 g were acidulated with 300 ml 4 M hydrochloric acid and 2 M sulfuric acid, respectively. After the acidulations, the entire reaction mixtures were filtered through a 250-mesh metal wire to recover the fibers and other solid materials. The recovered materials were also washed with some acetone, to remove any traces of tall oil. In addition, the isolated materials from the sulfuric acid acidulations were also washed with 4 M hydrochloric acid to dissolve calcium sulfate crystals.

The main reason for the use of the two acidulation systems above was that 5 (of 16) isolated fiber materials also contained varying amounts of resin-type material. At least part of this seemed to be acid salts, possibly due to incomplete acidulation. For comparison, the less successful hydrochloric acid acidulations were repeated with sulfuric acid. In addition, a large number of other soaps were treated with sulfuric acid (cf. Section 3.7).

All the isolated fibers and other solid impurities were determined gravimetrically, and subjected to examination and photographing under microscope. Color tests for the extractives (Sudan orange) and iron were also conducted for selected materials under the microscope.

As will be described in Section 3.7, several isolated materials contained some resin (or defoamer) type material. These were additionally characterized by FTIR. There were also some isolated materials that seemed to contain crystalline salts or related substances. A selection of them were analyzed for sodium and various non-process elements.

3 RESULTS AND DISCUSSION

The main results from the extensive analytical work are compiled in several appendices, and are briefly discussed in this Chapter, with attempts to find any correlations between process conditions and soap composition (impurities in the soaps). Based on these findings, the main conclusions are presented in Chapter 4.

Some notes on the appendix tables and sets of images need to be given, before the closer look at the results in Sections 3.1–3.7:

Appendix 1 (4 tables) gives the main results for the soap compositions, listing the contents of the dry solids, tall oil, sodium and potassium, non-process elements (NPEs), turpentine, lignin, polar carboxylic acids, and fibers. The Appendices 1a and 1c give the total NPE figures; more detailed data for the analyzed eight elements are given in the Appendices 1b and 1d. They also show which soap samples were analyzed by laser ablation technique for the distribution of the non-process element. As already pointed out in Chapter 2, it was not reasonable to analyze all the samples for all the impurity types (particularly lignin and polar carboxylic acids were analyzed for a few samples only).

Appendix 2 (1 table) gives the composition of the isolated tall oils on the group levels (share of fatty acids, resin acids, suberin acids, and neutral compounds), comparing the spontaneously separated oil and total tall oil (the latter one includes tall oil from the lignin phase). Appendix 3 (5 tables) gives more detailed composition of the same tall oil samples, listing the contents of c. 40 main compounds.

Appendix 4 gives 18 examples on the distribution of different non-process elements in different soap samples (on their frozen surfaces). The high number of examples is justified by a number of factors, especially by the variation from soap to soap and the novelty of the method (not applied to the soap analysis before).

Appendix 5 shows altogether 70 microscope photos of fibers and other solid impurities (dirt) isolated from numerous soap samples. The closer study of all these impurities has resulted in some of the main findings in this work, explaining the need to present all these photos. Finally, Appendix 6 gives some key process information from the soap separation and handling at the mills.

3.1 Tall oil – contents and composition

The tall oils were isolated and analyzed by GC/MS (Figs. 1–2), after acidulation with hydrochloric acid (Apps. 1–3). In separate experiments, it was also checked that the choice of the acidulation chemical (sulfuric or hydrochloric acid) does not affect the composition of the resulting tall oil.

According to review in this project (Niemelä 2003), tall oil contents of the soaps is typically 45–55%. The current figures for 22 soaps vary from 44.7 to 61.6%, with an average of 53.4%. This is also in a good agreement with recent data by Räsänen (2003) who found 47.7–57% contents for 7 soap samples.

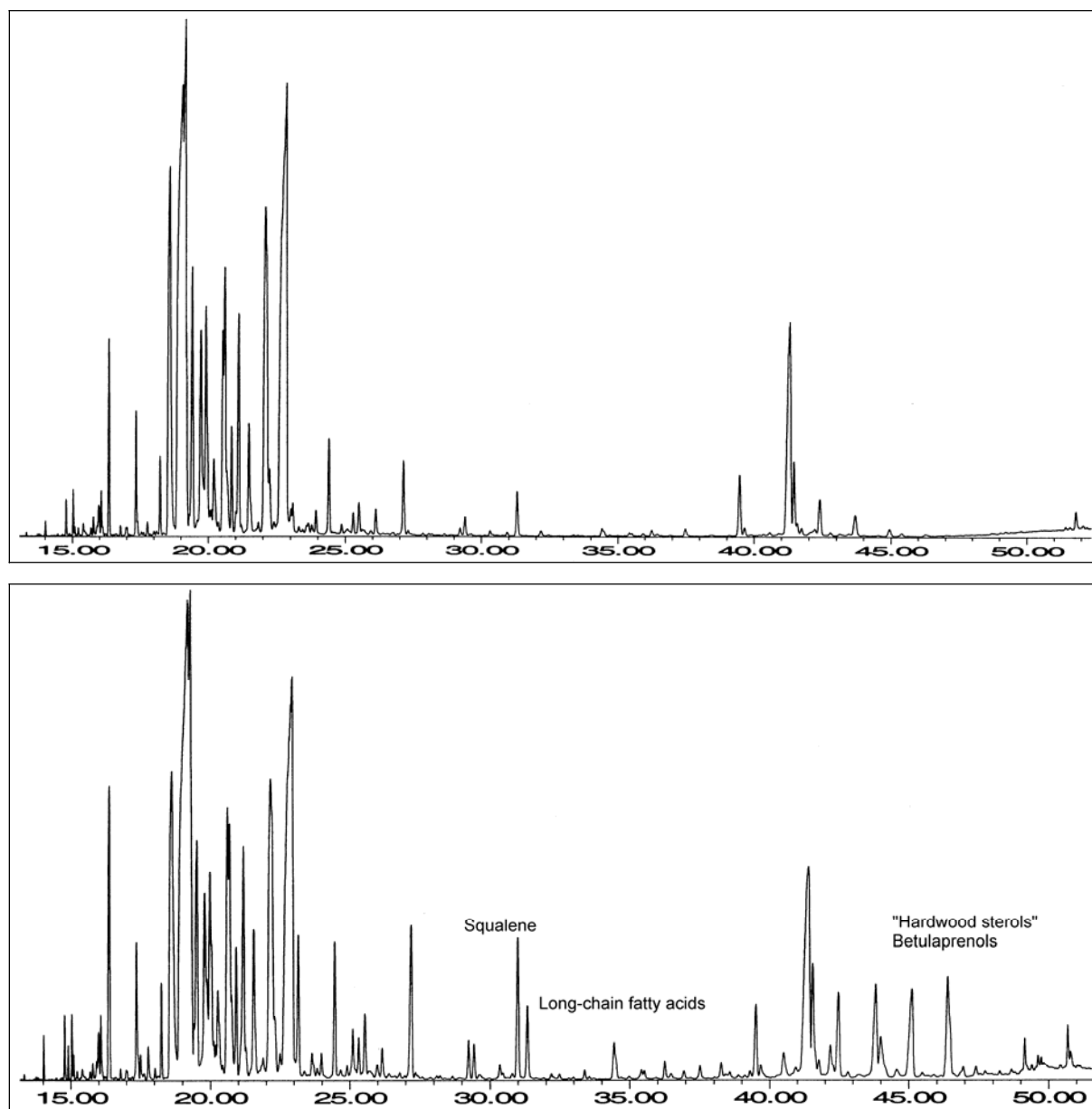


Fig. 1. Typical examples of GC analysis of tall oil from softwood (top) and mixed (hardwood + softwood, bottom) black liquor. The contribution of hardwood is readily indicated by the peaks of long-chain fatty acids, and certain neutral compounds like squalene, many sterols, and betulaprenols.

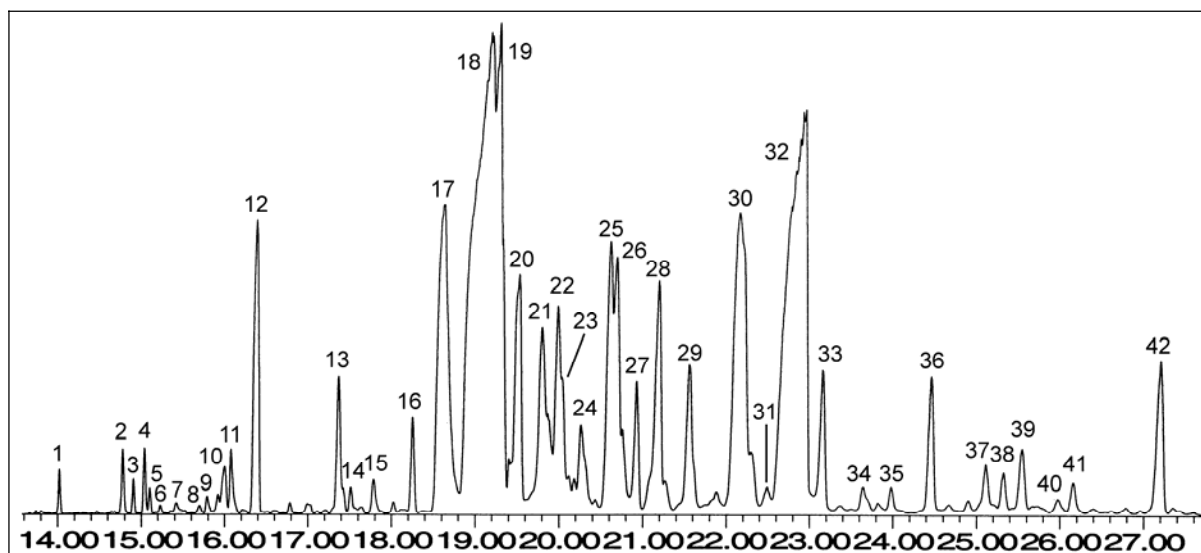


Fig 2a. Gas chromatographic separation of the trimethylsilylated compounds in a tall oil derived from a mixed (hardwood + softwood cooking) soap, retention time area of 14–27 min. 1, myristic acid; 2, methylmyristic acid, 3, a pentadecenoic acid; 4, a neutral diterpene; pentadecanoic acid; 6–9, neutral diterpenes; 10–11, palmitoleic acid isomers; 12, palmitic acid; 13, methylpalmitic acid; 14, a heptadecenoic acid; 15, heptadecanoic acid; 16, a neutral diterpene; 17, linolenic acid; 18, linoleic acid; 19, oleic acid; 20, stearic acid; 21, linoleic acid isomer 1; 22, linoleic acid isomer 2; 23, linolenic acid isomer; 24, linoleic acid isomer 3; 25, linoleic acid isomer 4; 26, pimaric acid; 27, sandaracopimaric acid; 28, isopimaric acid, 29, palustric + levopimaric acids; 30, dehydroabietic acid; 31, pentadecanedioic acid (?); 32, abietic acid; 33, eicosanoic acid; 34, a hydroxyresin acid; 35, dehydrodehydroabietic acid; 36, neoabietic acid; 37, heneicosanoic acid; 38, 1-docosanol; 39, a hydroxyresin acid; 40, a lignin dimer; 41, a hydroxydehydroabietic acid; and 42, docosanoic acid.

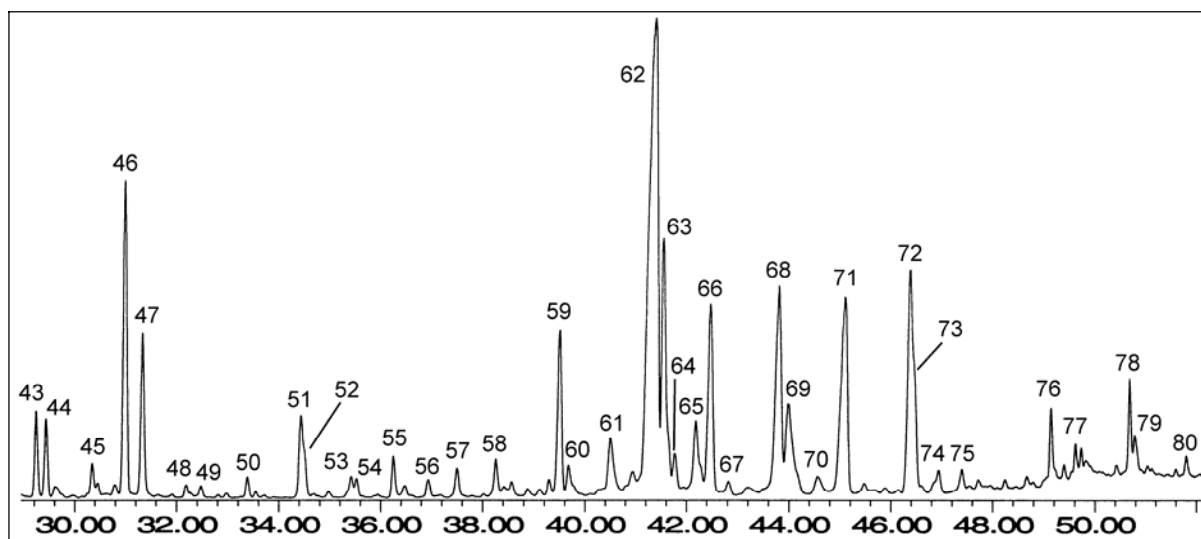


Fig 2b. Continuation of Fig. 2a, showing the retention time area of 28–55 min. 43, tri-cosanoic acid; 44, 1-tetracosanol; 45, nonadecanedioic acid; 46, squalene; 47, tetra-cosanoic acid; 48, eicosanedioic acid; 49, a long-chain hydroxy fatty acid; 50, penta-cosanoic acid; 51, heneicosanedioic acid; 52, a higher homolog of 53; hexacosanoic acid; 54, a sterol (?), 55, docosanedioic acid; 56, a dihydroxy fatty acid; 57, a lignin dimer; 58, a betulaprenol; 59, campesterol; 60, a sterol; 61, a betulaprenol; 62, β -sitosterol; 63, β -sitostanol; 64, a betulaprenol; 65, lupeol; 66, cycloartanol; 67, a sterol; 68, 24-methylenecycloartenol; 69, a betulaprenol; 70, a sterol; 71, citrostadienol; 72, betulinol; 73, methyl betulinate; 74 a sterol; 75–79, betulaprenols; and 80, a sterol (?),

The tall oil contents in the soaps apparently mainly depend on the final black liquor washing (decantation) conditions and do not correlate with the pulping conditions or raw material. It looks that a few mills can achieve up to 60% tall oil contents in the soap fed to the acidulation reactors.

The composition of the tall oils derived from different soaps can vary to a certain extent (Apps. 2–3). Three main types of the tall oils can readily be distinguished, based on the relative amount of neutral compounds:

- Neutral compound content c. 10% (8–12%), typical for 100% softwood soap.
- Neutral compound content c. 15–22%, typical for mixed soap, depending on the share of hardwood and softwood.
- Neutral compound content nearly 30%, typical for pure or almost pure hardwood soap (with tall oil resin added into the cook).

The main neutral compound in the tall oils always seems to β -sitosterol, characteristic of both softwood and hardwood. In addition to β -sitosterol, there are there numerous neutral compounds characteristic of hardwood (birch) only, and their presence readily indicates (Fig. 1) the source tall oil (or mixture). These especially include squalene, betulaprenols, and different sterols, such as lupeol, betulinol, and methyl betulinate.

The highest contents of resin acids were naturally found for the pure softwood-derived tall oils; figures up to 40% were recorded. Many mills use at their hardwood cooking lines some resin soap to improve soap separation, which artificially increases the content of the resin acids in the corresponding soaps. Thus, in these cases the resin acid content of the soaps is somewhat higher than expected from the raw material use.

The composition of the resin acid fraction (App. 3) is in each case typical for pine and spruce woods. Only relatively small amounts of any oxidized resin acids were found.

The content of fatty acids in the tall oils varied from c. 48 to 56%; higher share of hardwood in the raw material increases the amount of fatty acids. Oleic, linoleic and linolenic acids are always the dominating fatty acids, although some isomeric compounds are also present. Their more detailed structure determinations were now outside the scope of this study.

Small amounts (c. 0.2–1%) of so-called suberin acids were also found in the tall oils. These compounds are long-chain hydroxy acids or dicarboxylic acids (e.g. peaks 45, 48, 49, 51 and 55 in Fig. 2b), typically derived from bark (especially from birch outer bark).

The comparison of the spontaneously separated and total tall oils usually reveals only minor differences, indicating that the tall oil in the lignin phase has very much the same composition as the readily separated tall oil.

3.2 Non-process elements

Sulfate soap is known to effectively scavenge calcium and other non-process elements from black liquor during soap separation (e.g. Magnusson et al. 1980, Koistinen 1991, Vuorikari 1992, Järvinen 1996, Ellis et al. 1998, and Kukkola 1998; cf. Niemelä 2003). For example, up to 50–70% of black liquor calcium has frequently been reported to move from black liquor to soap.

Too high concentrations of these elements (especially calcium) are known to be detrimental for soap quality. Therefore, a number of non-process elements were now analyzed in all of the soap samples, and their distribution patterns were investigated (in order to clarify the nature of the compounds they are bound to).

The total amount of the eight investigated non-process elements varied from 0.7 to 7.4 g/kg soap. It is reasonable to expect that the variation correlates with the variation of these compounds in the corresponding black liquors (not analyzed). This, in turn, may depend on numerous things (raw material, use of process chemicals and make-up chemicals, removal of dregs and lime mud, and many others). It is also possible, for example, that different amounts of the main tall oil compounds (fatty acids, resin acids, neutrals) in the soap affect the distribution of certain non-process elements between black liquor and soap. However, it is not possible to make any reasonable conclusions on this question.

In all, 18 investigated soap samples represented acidulation feed soaps. Of these, most (10) had the NPE level in the range of 2–3 g/kg, five were below 2 g/kg, and only three were above 3 g/kg (3.1, 3.5, and 7.4).

Calcium. – In each case, calcium was the dominating non-process element, with a typical content of c. 0.8–2.8 g/kg. There were only three figures below 0.8 g/kg and two figures above 2.8 g/kg. The highest figures (5.7 and 6.5 g/kg) were found in feed liquor and acidulation feed soaps from the Kotka mill, although the intermediate liquor soap from the same mill contained calcium only 1.4 g/kg. Generally, no trend can be recognized between the pulping raw material (softwood, mix) and calcium content in the soap. For example, there are pure softwood mills with low, moderate, and high calcium contents, whereas most of the soaps from mixed raw material mills have low to moderate calcium contents (typically around 1.5 g/kg).

Magnesium. – The content of magnesium in the soaps varied a lot, from c. 30 up to 1200 mg/kg. A typical range seemed to be roughly from 300 to 750 mg/kg; only eight figures were higher than this. At many mills (e.g. Joutseno, Sunila, Imatra, and Varkaus) the magnesium content varies only little between the soaps from different sampling points. At some other mills (e.g. Kymi) there is, however, much deeper variation. In some cases, this may reflect the use of magnesium sulfate at hardwood lines during oxygen delignification.

Silicon. – Most of the silicon concentrations were in the range of 100 to 400 mg/kg, although figures up to 730 mg/kg were occasionally recorded. In most cases, the silicon contents within different soaps in one mill were relatively constant, although some deviating cases (e.g. Enocell, Kymi) could also be found.

Manganese. – Most of the recorded manganese contents were below 200 mg/kg, although the highest figures were 430 mg/kg. It looks that there are no distinct raw material based differences in the manganese contents of the soaps.

Iron. – All the soap samples contained some iron, although the concentrations ranges varied from 3 to 300 mg/kg. Only in two cases, however, figures more than 100 mg/kg were recorded. It is possible that there have been some solid iron particles (e.g. rust) in these samples. Their presence of iron could also be demonstrated by a coloring reaction which revealed that most of iron is typically attached into small particles around fibers (Fig. 3).

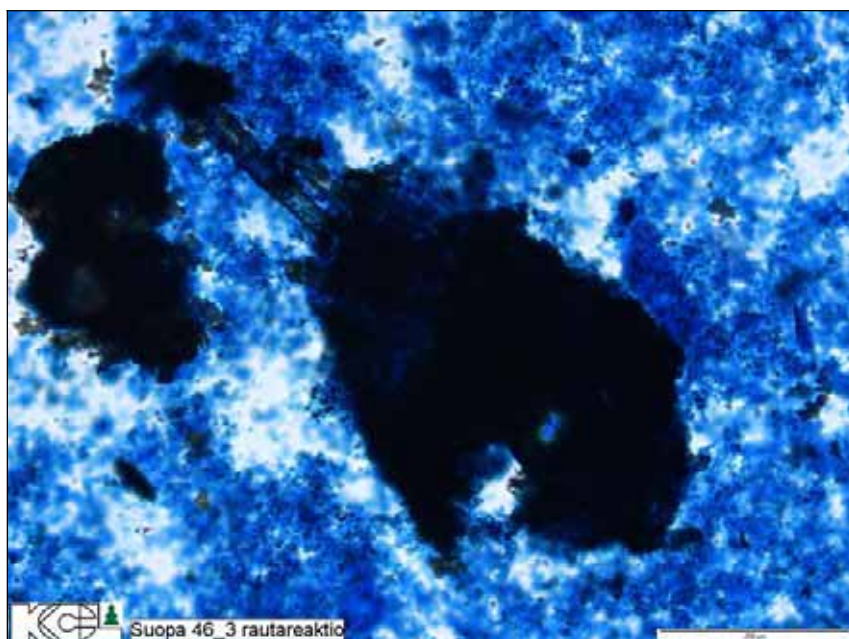


Fig. 3. Example of the detection of iron in soap solids by a coloring reaction.

Aluminum and zinc. – The concentrations of aluminum and zinc were typically in the ranges of 15–50 and 20–100 mg/kg, respectively. Occasionally, however, higher zinc contents (up to 270 mg/kg) were found.

Phosphorus. – The content of phosphorus in the soap samples varied from c. 70 to 600 mg/kg, although the most typical figures seemed to be c. 150–300 mg/kg. No clear differences seem to be derived from the use of different wood raw materials.

Distribution of the non-process elements; their compounds. – Very little is so far known on the compounds (e.g. inorganic or organic salts) formed by the non-process elements in the soaps, due to analytical problems. For example, it is not readily possible to isolate possible crystals or precipitates of the non-process element compounds from the soaps for a closer characterization. Many metals can naturally be also present in the

form of fatty acid or resin acid salts, and their specific isolation would also be very challenging.

Therefore in this work, a novel approach was applied. This was based on laser ablation of frozen surfaces of soap samples, followed by the monitoring of the evaporated (selected) elements. The laser beam was allowed to travel short distances on the soap surfaces, and relative distribution patterns of the elements were recorded. If two or more elements have similar or identical distribution patterns, it is reasonable to assume that they form compounds together, or occur in the same co-precipitates.

Appendix 4 shows a few examples of dozens of this type of analyses now conducted. The results are of more general importance and are therefore discussed without describing the soap samples (mills) in more detail.

Calcium was one of the main elements analyzed this way, due to its typically high concentration in the soaps. Appendix 4a shows four different examples where the distribution patterns of calcium are compared with those of potassium and manganese. As potassium is a water-soluble element, it can be assumed to be present in the black liquor remains in soap, or as a salt with fatty and resin acids. Therefore, distribution patterns free of big peaks or agglomerates should be seen for potassium by the applied technique, and this also seemed to be the case. The patterns for calcium were, to some extent, either quite similar with those of potassium, or occasionally, more pronounced calcium contents were found in some areas. In some cases, the areas with higher amounts of calcium also contained higher amounts of potassium and manganese.

From these observations it can be concluded that at least most of the calcium is relatively evenly distributed in the soap, which makes it reasonable to assume that it typically forms salts with resin and fatty acids, instead of forming calcium carbonate or other inorganic calcium salts.

The simultaneous determination of magnesium and silicon reveals totally different distribution patterns, thus ruling out possibilities of magnesium silicates (App. 4b). The distribution curve for silicon was usually found to be almost identical for each soap sample, and this feature remained somewhat puzzling. There is even a possibility that there is some kind of instrumental background that could not fully controlled. In any case, it is evident that the magnesium distribution patterns are totally different, and that it is possible to detect precipitates or compounds where magnesium is clearly enriched. It also looks that such enrichments may also contain other elements, such as aluminum and phosphorus (Apps. 4b and 4c).

Aluminum, zinc and phosphorus were frequently found to give identical or nearly identical distribution patterns (Apps. 4d and 4e). This should leave no doubt that aluminum and zinc occur in soap (apparently also in black liquor) as insoluble phosphates. In many cases, other phosphate compounds must also be present as the total phosphorus content in the soaps was relatively high.

3.3 Defoamers

So far, nothing has apparently been published on the possible effects of different defoamers on the separation and quality of sulfate soap. As discussed in Section 3.2, there remained a possibility that at least part of silicon in the soaps could be linked to the presence of silicone-based defoamers.

Therefore, five soap samples with the highest silicon contents (cf. App. 1) were extracted with hexane, known to recover silicones (Auterinen 2000). The extracts were concentrated and analyzed by FTIR. None of the extracts could be confirmed to contain silicones, indicating that their concentrations must be very low, if present at all (no attempts were now made to determine the detection limit for this method). Instead, the extracts were shown to contain numerous other types of compounds, like sterols and other neutral extractives.

In another attempt, the same soap samples were spiked with a silicone defoamer (calculated to double the silicon content) and the spiked samples were subjected to the laser ablation analyses for silicon (cf. Section 3.2). This did not change the recorded distribution patterns of silicon, indicating that silicone defoamer was evenly distributed in the soap after spiking. Alternatively, the determination was hampered by the strange instrumental background effect that could not be fully controlled or understood.

As will be discussed in Section 3.7, it could occasionally be shown that some silicone defoamer can be present in the solid material isolated from soaps after acidulation.

3.4 Turpentine

Although it seems to be well-known that varying amounts of turpentine can be present in soap (cf. Niemelä 2003), only a few concentration figures have apparently been published so far.

In this work, turpentine was analyzed by two methods: qualitative analysis by extraction and GC/MS (Fig. 4), allowing a detailed identification of turpentine compounds and other hydrocarbons, and quantitative analysis by head-space GC (to quantify the main monoterpenes).

As can be seen in Figs. 4–5, the GC/MS analyses revealed the presence of varying amounts of monoterpenes, sesquiterpenes, diterpenes, and squalene. The latter compound is characteristic of hardwood so its amount reflects the raw material use. Although a large number of soap samples were analyzed this way, none of them were found to contain hydrocarbons of industrial (i.e. not from wood) source. For example, no compounds apparently derived from the defoamer preparations were detected.

The turpentine concentrations varied from 0.1 to 20 g/kg and were naturally the highest for the pure softwood soaps. In many cases it could be seen that the turpentine contents were lower in the intermediate liquor soaps than in the weak liquor soaps. Very little is known on the effect of turpentine on the soap separation.

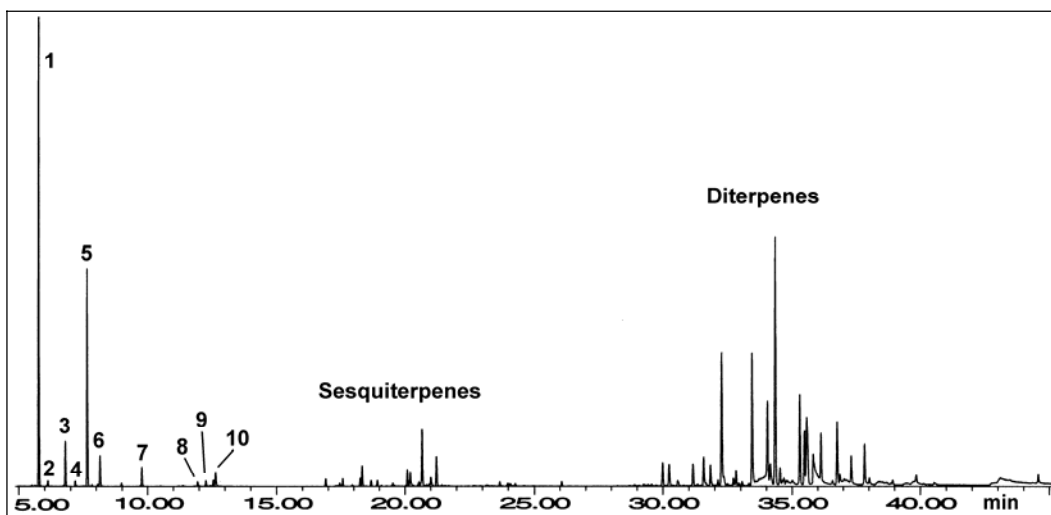


Fig. 4. Separation on an HP-5 column of turpentine compounds in a hexane extract of pure softwood-derived sulfate soap. 1, α -pinene; 2, camphene; 3, β -pinene; 4, myrcene; 5, 3-carene; 6, dipentene; 7, terpinolene; 8, borneol; 9, 4-terpineol; and 10, γ -terpineol. No attempts were now made to identify the numerous sesquiterpenes and neutral diterpenes (hydrocarbons, alcohols, and aldehydes) in more detail.

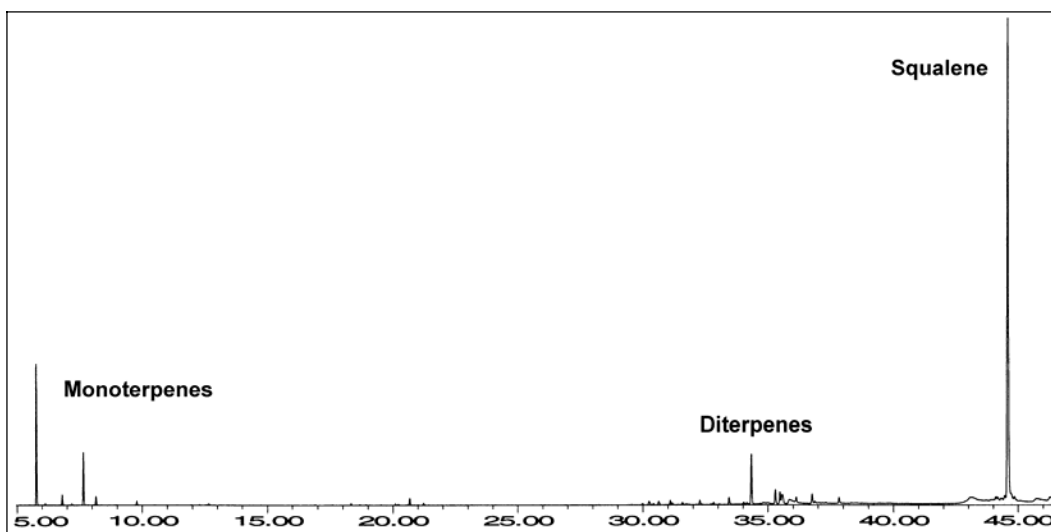
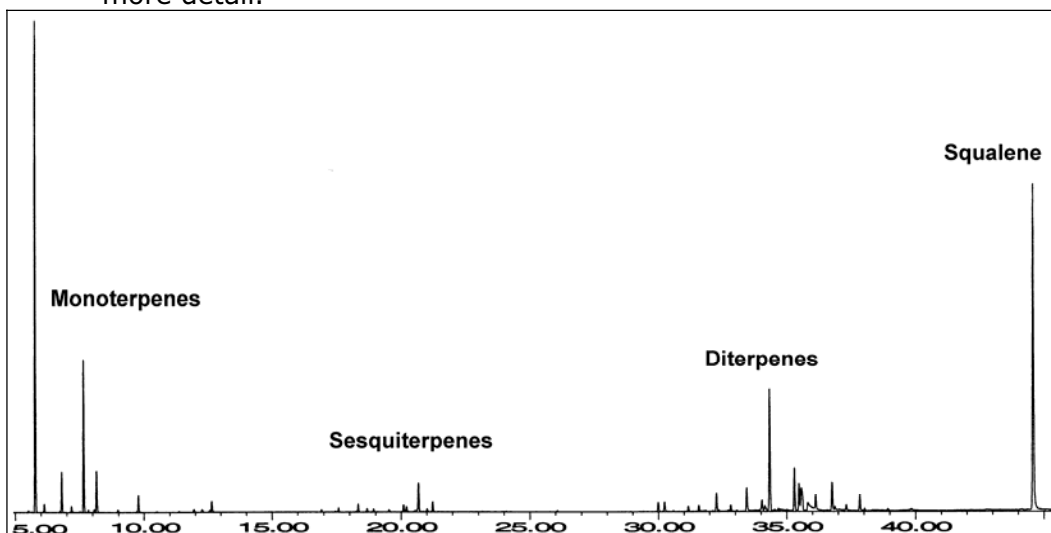


Fig. 5. Typical distribution patterns of hydrocarbons in soaps with minor (above) and stronger (minor) contributions of hardwood as a raw material.

3.5 Lignin

The lignin content was determined for 21 soap samples, giving the figures of 4–11 g/kg which are on the known and expected levels. The amount of lignin in the acidulation feed soaps is known to depend on the extent of soap washing (black liquor decanting), and is apparently not correlating with the raw materials or cooking conditions.

Although the recorded lignin concentrations may sound low, it is known that they may have strong effects on the separation of different phases after soap acidulation.

3.6 Polar carboxylic acids

Hydroxy carboxylic acids and related compounds were now analyzed in several soap samples (Fig. 6), for two main reasons. First, they have never before been studied in soap samples as impurities in any detail. Second, it was of special interest to check if any calcium-complexing acids could be found in enriched amounts (compared with other acids) as this would bring new information on the nature of calcium compounds in the soaps.

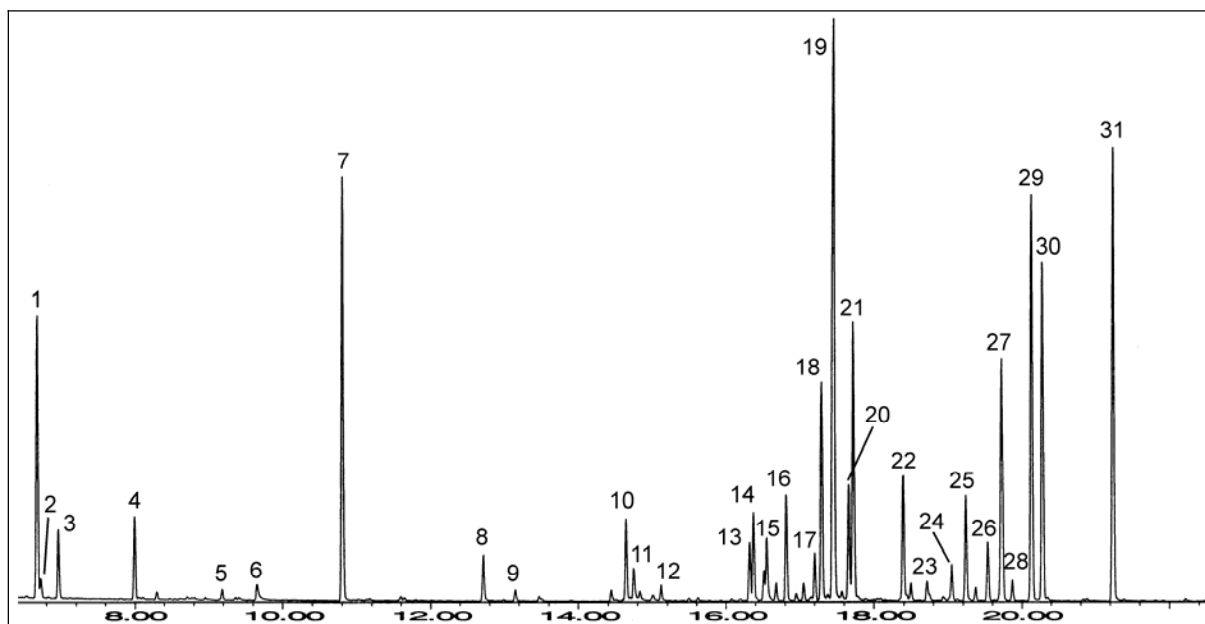


Fig. 6. Separation on an HP-5 column of trimethylsilylated hydroxy acids and other polar compounds in mother liquor derived from hydrochloric acid acidulation of a soap sample. 1, lactic acid; 2, 2-hydroxy-2-methylpropanoic acid; 3, glycolic acid; 4, 2-hydroxybutanoic acid; 5, a 2-hydroxypentenoic acid; 6, 3,4-dihydroxybutanoic acid (lactone); 7, phosphate; 8, xyloisosaccharinic acid (lactone); 9, 2,4-dihydroxybutanoic acid; 10, 2,5-dihydroxypentanoic acid; 11, 3-deoxypentonic acid (lactone); 12, unknown hydroxy acid (lactone); 13–17, monosaccharides (both furanose and pyranose forms); 18, α -glucoisosaccharinic acid (1,4-lactone); 19, β -glucoisosaccharinic acid (1,4-lactone); 20, α -xylopyranose; 21, xylitol (internal standard); 22, β -xylopyranose; 23–26, monosaccharides (mainly furanose forms); 27, α -mannopyranose; 28, unknown hydroxy acid; 29, α -glucopyranose; 30, β -mannopyranose; and 31, β -glucopyranose. The monosaccharides have been liberated from polysaccharides during acidulation and do not represent original black liquor or soap constituents. Low relative amounts of 2-hydroxybutanoic and xyloisosaccharinic acids indicate that this soap sample is derived from a softwood kraft pulp mill.

The applied analytical procedure was successful and resulted in the detection and identification of a large number of hydroxy acids and other polar compounds in the soap samples (Fig. 6).

A closer look at the acids indicates and their known amounts (Niemelä and Alén 1998) in black liquors indicates that:

- All the identified acids are typical black liquor compounds, mainly derived from carbohydrate degradation reactions during cooking.
- There are certain differences between pure softwood soaps (their acids) and those present in mixed soaps, i.e. the contribution of the hardwood raw materials can be seen
- The relative amounts of all acids are very much in the line with their presence in black liquors, i.e. no enrichment for known strong calcium complexants is evident.
- The monosaccharides present in the mixture do not represent original black liquor compounds. Instead, they have apparently been formed from polysaccharides during the soap acidulation.

There is, however, one distinct difference when the present chromatogram example (Fig. 6) is compared with the chromatograms from black liquors: substantial phosphate peak (peak no. 7). In the black liquor chromatograms, the phosphate always gives a tiny peak just visible. Its big size now indicates the enrichment of aluminum and zinc (and perhaps some other) phosphates, as already discussed in Section 3.2.

The amount of phosphorus calculated from the phosphate contents (as analyzed by GC/MS) was usually in a good agreement with the total phosphorus contents determined by ICP (App. 1). This indicates that most or all of phosphorus is in the form of phosphate.

The total concentrations of the polar carboxylic acids in the soaps varied from 6 to 19 g/kg, thus being slightly more abundant than lignin. As fully water-soluble compounds they can hardly cause any problems during soap acidulation. In the Appendix 1, only the total concentrations for these acids are now given, i.e. there are no separate tables showing the concentrations of the individual acids.

In addition to the above hydroxy acids, there may be some other type of polar compounds (like oligo- or polysaccharides) present in the soap. It was not now reasonable, however, to look at them any closer.

3.7 Fibers and other solid impurities

The isolation and detailed characterization of fibers and "dirt" from the numerous soap samples resulted in a number of unexpected findings, some analytical problems and challenges, and new results, differing from some previously published results. Altogether, these findings also made it necessary to re-consider the objectives or problem-setting of the current work, and to use more resources for certain further analytical work and characterization. The following list summarizes the main findings:

- The nature of the isolated impurities may vary a lot from mill to mill.
- The amount of fibers in the isolated materials vary a lot, from almost traces to nearly 100%.
- In nearly each case, the amount of the isolated material (when the acidulation was successful) was lower (below 5 g/kg) than expected.
- Acidulation with sulfuric acid always produces calcium sulfate crystals which increase the amount of the isolated material, violating quantitative results.
- Acidulations with hydrochloric or sulfuric acid may leave some soap (especially calcium salts) unreacted, causing risk of increased amount of the isolated material.
- Other impurities include different resin-type or oil/chemical-looking materials (like defoamers) that could be only partially characterized.
- Occasionally, solid metal salts (organic or inorganic) are also present.

The above findings are discussed in more detail below, starting by a more general discussion (Section 3.7.1), followed by a more detailed mill-by-mill discussion (Section 3.7.2). As a part of the work, hundreds of microscope images were taken of which a representative selection will be provided.

One of the main conclusion from the current characterization work is to state that *it is always necessary to subject the fibers isolated from soap to microscopic characterization before making any further conclusions on their contribution to soap separation and quality.*

3.7.1 Overview; types of impurities

Varying amounts of solid impurities were isolated from each soap sample, by acidulation with hydrochloric or sulfuric acid, followed by filtering thorough a 250-mesha metal fire. The amount of proper fibers in the isolated materials varied a lot (cf. Section 3.7.2), indicating incorporation of varying amounts of different other types of materials. The other materials included unreacted soap (especially calcium salts), liquid or low-viscosity resin-type or oil-type particles or agglomerates (mainly organic), inorganic crystals, and other materials.

Attempts were made to separate and characterize the different materials by different means, such as by FTIR. This way it could be found confirmed that there may be some unreacted soap present, and that clearly neutral extractives (such as betulinol) can be found. In many cases, however, the exact nature of these organic-looking materials remained unknown.

A specific feature, possibly previously known but apparently not mentioned in any publications or reports, is the formation of calcium sulfate during sulfuric acid acidulation. The resulting white crystals may form separate particles, or precipitation may also occur around fibers (Fig. 7). It is evident that this type of precipitates increase the amount material reported as "fibers" or "dirt", if not removed.



Fig. 7. Calcium sulfate crystals around fibers isolated from soap.

There is no risk of calcium sulfate formation if the acidulation is conducted with hydrochloric acid. Alternatively, the materials isolated (after sulfuric acid acidulation) on a screen should be washed with hydrochloric acid, to dissolve calcium sulfate.

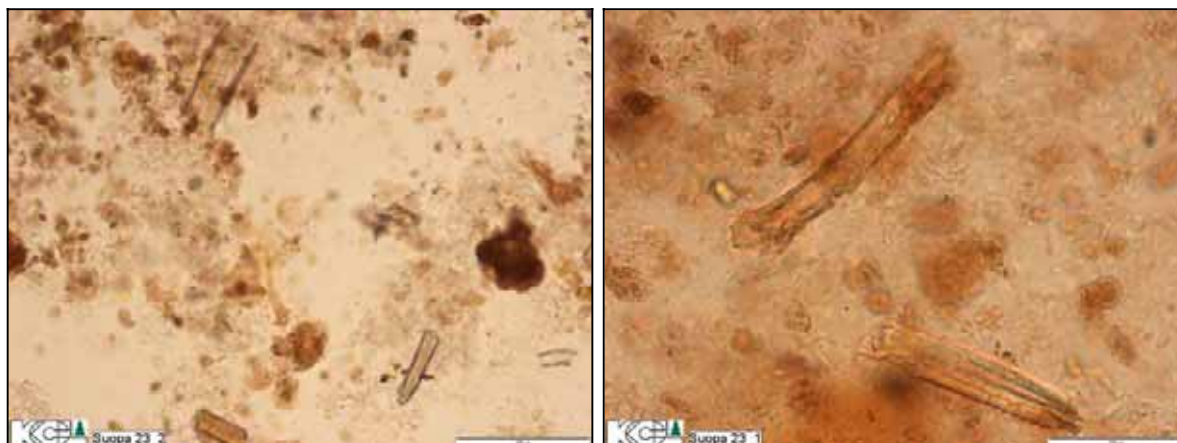
In addition to calcium sulfate, other type of metal salts or compounds could occasionally be detected, often clearly incorporated with the fibers. A number of fiber/dirt samples (isolated from different soap) were now analyzed for sodium and selected non-process elements (Table 2). Iron and calcium were the main non-process metals, although some barium and silicon could also be found. It is most likely that iron occurs mainly in the form of simple rust, whereas calcium has been bound to fatty and resin acids. Only in one case (Table 2), moderate amounts of sodium were recorded. This must refer to the presence of unreacted soap.

Table 2. Contents (g/kg) of sodium and certain non-process elements in the solid materials (fibers + dirt) isolated from selected soap samples. IL, intermediate liquor, WL, weak liquor.

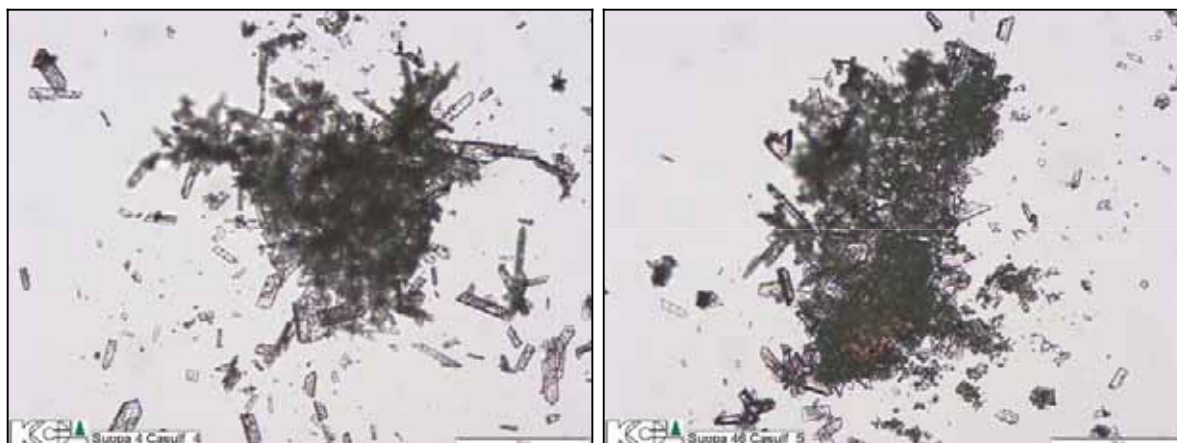
Mill, soap	Al	Ba	Ca	Fe	Mg	P	Si	Na
Rauma, acidulation feed	0.2	1.3	4.9	71	0.3	<0.1	3.1	0.2
Kymi, intermed. liquor	0.4	0.6	<0.1	82	<0.1	<0.1	3.0	0.1
Tervasaari, SAP soap	0.8	2.8	2.9	8.9	<0.1	<0.1	16	4.6
Kotka, weak liquor	0.5	6.9	42	80	<0.1	<0.1	9.3	0.2
Varkaus, intermed. liq.	<0.1	0.4	0.9	8.5	<0.1	<0.1	2.3	5.3
Joutseno, acidul. feed	1.1	0.5	0.2	93	2.1	<0.1	8.5	0.1
Kaskinen, acidul. feed	<0.1	0.2	0.7	0.3	0.4	<0.1	2.0	90
Kemijärvi, intermed. liq.	<0.1	0.5	79	30	<0.1	<0.1	4.0	2.7

3.7.2 Microscopic examination of the isolated impurities

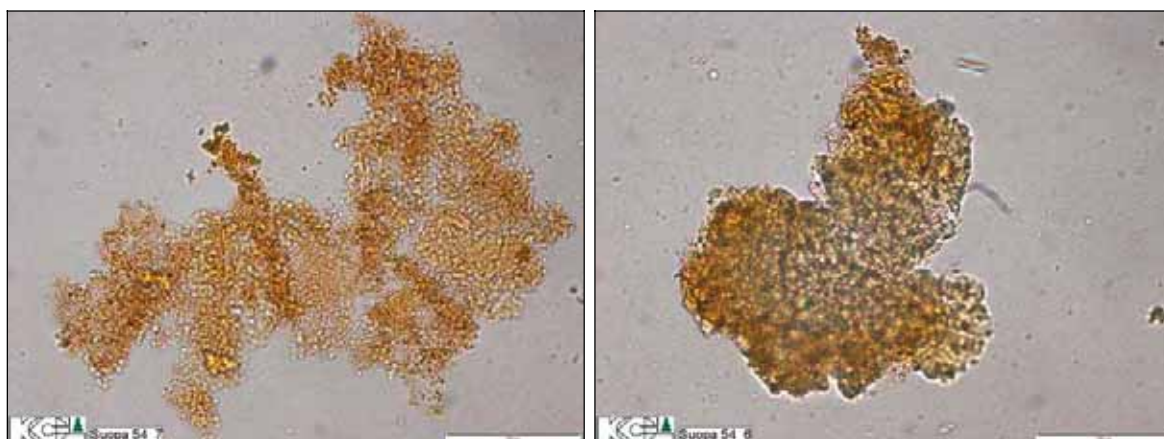
During the course of this work, hundreds of photographs were taken from the solid materials isolated from numerous soap samples. Usually, this type of examination revealed if there is any unreacted soap present (Fig. 8) or if the washing of the calcium sulfate crystals has been incomplete (Fig. 9), or other general peculiarities (Fig. 10).



Figs. 8a and 8b. Examples of fibers entrapped in incompletely acidulated soap.



Figs. 9a and 9b. Calcium sulfate crystals partially covering fibers (sulfuric acid acidulation, *incomplete* washing of the crystals with hydrochloric acid).



Figs. 10a and 10b. Resin/oil-type particles isolated from a hydrochloric acid treated soap (scale = 100 μ m). The material may be agglomerate of neutral hardwood extractives.

In this section, comments will be given on 70 reproduced photographs, giving a detailed demonstration on the wide variability of the fibers and dirt in the isolated material. It will also be seen how challenging task it is to correlate the nature of the isolated materials with any process conditions (pulping, soap separation) or any other soap quality characteristics.

Joutseno (App. 5.1). – The soaps from the Joutseno's weak liquor and acidulation feed soaps contained 4.1 and 0.9 g/kg fibers + dirt, respectively. In both cases, only a part of the material was fibers or fiber fragments. These fiber fragments are apparently material that is sometimes called "microfibers". In addition to the fibrous material, there are some resin-type, extractives-related particles present. Under the microscope, glassy polarizing crystals could also be recognized. A strong iron color reaction was demonstrated; it appeared that many small very dark spots gave the strong color reaction, possibly suggesting the presence of rust or other iron material.

Kaskinen (App. 5.2). – The soaps from the Kaskinen's intermediate liquor and acidulation feed soaps (birch campaign) contained 1.9 and 4.9 g fibers + dirt, respectively. To a certain, the materials represent those isolated from the Joutseno's soaps, although the amount of the proper fibers is lower. There is apparently some calcium sulfate still present, although hydrochloric acid washing was carried out. Fat-related dark spots may be agglomerates of hardwood-derived neutral extractives.

Kemi (Apps. 5.3–5.4). – The soap from the Kemi's acidulation feed soaps contained 2.2 g/kg g fibers + dirt. Interesting is, however, that the same material isolated after the sulfuric acid acidulation and hydrochloric acid acidulation can differ a lot. In the latter case, almost pure softwood and hardwood fibers or fiber fragments can be seen. The nature of the dark spots (App. 5.3) was not fully characterized, although there may be some unreacted soap still present.

Rauma (App. 5.5). – The soaps from the Rauma's collecting tank and acidulation feed soaps contained 1.6 and 2.2 g/kg fibers + dirt, respectively. As demonstrated for the former one, there are both fibers or fiber fragments and resin/fat-type material present. Some calcium sulfate crystals can also be seen. The material gave a strong color reaction for iron.

Äänekoski (App. 5.6). – Only very little (07 g/kg) solid material could be isolated from the Äänekoski's soap, containing small amounts of fibers or fiber fragments. The crystal type materials may be calcium sulfate or calcium soaps of fatty acids.

Kaukas (Apps. 5.7–5.8). – The soaps from the Rauma's collecting tank and chemical plant soaps contained 2.7 and 2.4 g/kg fibers + dirt, respectively. Of these, the latter one formed a distinct fiber mat during the isolation; only some material of other type than fibers or fiber fragments could be found inside the mat. These included some crystals and resin/fat-type material. This type of distinct fiber mat was isolated from some other soap samples, too, as described later. The strong color reaction for the iron was demonstrated (for the two soap samples).

Kymi (Apps. 5.9–5.12). – In all, four different soap samples from the Kymi mill were characterized for the fibers + dirt, giving the concentrations from 0.3 to 6.7 g/kg. Of these, one was studied after hydrochloric acid acidulation and three after sulfuric acid acidulation. All these show fibers and fiber fragments of different sizes, including relative big fiber lumps. The dark particles seem to be mainly of organic nature that could not be characterized in more detail. This was especially present in the samples from the line 2. It is interesting, however, that this material was hardly present in the final acidulation feed soap where the amount of the solid impurities was the lowest, only 0.3 g/kg.

Pietarsaari (App. 5.13). – The material from the Pietarsaari acidulation feed was almost pure fiber and fiber fragments material, with only minor amounts of any resin/fat-type particles or agglomerates. Both hardwood and softwood fibers can be recognized.

Tervasaari (Apps. 5.14–5.16). – Different impurity materials were isolated from the three different soaps from the Tervasaari mill. The SAP soap contained 4.3 g/kg of the impurities, but only a part of that was fibers or fiber fragments. Some of the fibers formed nets or mats (App. 5.14 right), whereas there were also separate particles present. It is possible that there is also some unreacted resin (or calcium salts of fatty acids) present.

The kraft weak liquor soap from Tervasaari contained fibers + dirt 1.7 g/kg, also forming a net-type structure during filtration. In this structure, softwood fibers could be recognized, in addition to resin/oil-type material. The analysis of the acidulation feed soap revealed a high (25.7 g/kg) content of the fibers + dirt, apparently because of the presence of some unreacted soap.

Sunila (App. 5.17). – The Sunila's acidulation feed soap was analyzed for the solid impurities after hydrochloric and sulfuric acid acidulations; giving the contents of 1.1 and 2.6 g/kg, respectively. The material resembles very much of that from Joutseno; i.e. most of the fiber fragments are very small. There is apparently some unreacted soap also present. The color reaction for iron was very strong.

Enocell (Apps. 5.18–5.20). – Three soap samples from the Enocell mill contained 1.5–2.5 g/kg of fibers + dirt. In each case, these were mainly composed of unbroken and broken fibers that formed networks during the isolation. Only in one case (intermediate liquor soap, App. 5.19) the fiber network also contained moderate amounts of crystals and resin/fat-type agglomerates. Some of that may be neutral hardwood extractives.

Imatra (Apps. 5.21–5.22). – A very low concentration (0.9 g/kg) of the solid impurities were isolated from the Imatra's acidulation feed. This material was mainly fibers and fiber particles (forming a net), but some calcium sulfate crystals were still present

Kemijärvi (App. 5.23). – The two soap samples from the Kemijärvi mill yielded 2–2.3 g/kg of fibers and dirt, resembling very much those from Joutseno and Sunila (for example). In both cases, fibers and fiber fragments are present, in addition to other particles (including calcium sulfate crystals).

Kotka (Apps. 5.24–5.25). – Three soap samples from the Kotka mill contained 0.6–3.5 g/kg of fibers and dirt; the lowest figure was for the acidulation feed. Most of the material in the acidulation feed soap was composed of fibers and fiber fragments, with some dark-brown (black) spots. The spots were not, however, any rust particles as the color reaction for iron gave only moderate response.

It is noteworthy that the fibers + dirt content in the acidulation feed soap was so low, despite the presence of significant amounts of calcium in the soap (6.5 g/kg). This means that all the calcium salts of fatty acids (if present) were liberated during the conducted hydrochloric acid acidulation. Also, the use of this acid had prevented the formation of any calcium sulfate crystals, so often recognized during the sulfuric acid acidulation. Instead, it looks that at least some calcium sulfate crystals were formed during the treatment of the feed liquor and intermediate liquor soaps, resulting in the higher amounts of fibers + dirt.

Oulu (App. 5.26). – The acidulation feed soap from the Oulu mill contained 1.3 g/kg of fibers + dirt. Most of the material was fibers, with some resin/oil-type spots. In this case, the FTIR analysis clearly showed that these spots contain silicone defoamer (Fig. 11).

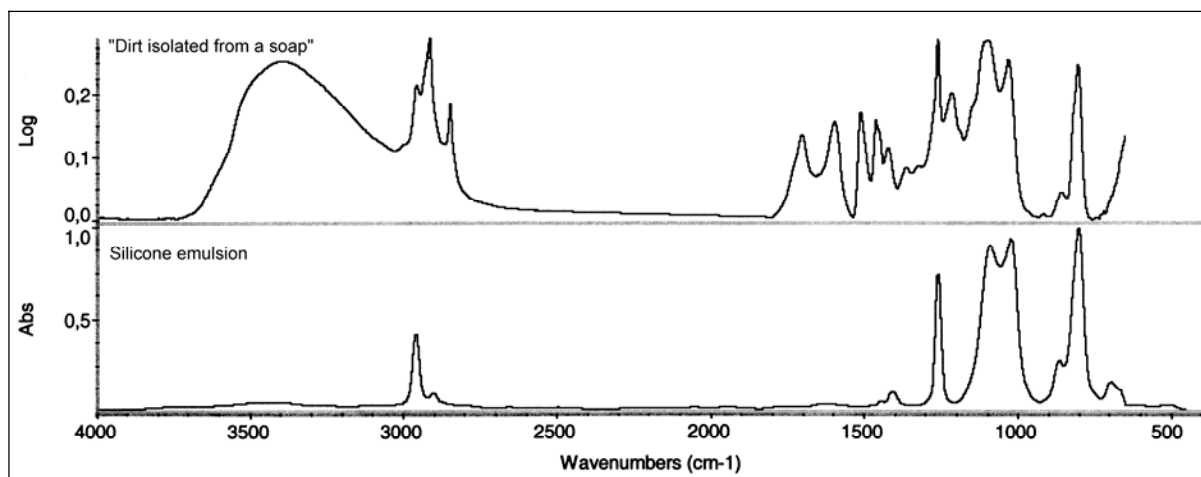


Fig. 11. FTIR spectra of brown spots from the solid impurities isolated from the Oulu soap (upper panel), and a reference silicone emulsion. The presence of some defoamer in the soap material is evident. Some lignin peaks can also be recognized.

Varkaus (App. 5.27–5.29). – Three soap samples from the Varkaus mill contained 1.9–8 g/kg of fibers + dirt; the highest amount was found in the intermediate liquor soap. The isolated materials contained varying amounts of fibers, although all the samples were somewhat different. A distinct fiber mat was recovered from the feed liquor soap, whereas the intermediate liquor soap material also seemed to contain unreacted soap (possibly calcium salts). The acidulation feed soap fibers were covered,

in a distinct way, by some resin/fat-type materials. That may include both lignin and unreacted soap.

Veitsiluoto (Apps. 5.30–5.32). – Three analyzed soap samples from the Varkaus mill contained only 0.5–3.2 g/kg of fibers + dirt; usually the proper fibers were the dominating materials. In the acidulation feed soap, exceptionally clean (and unbroken) hardwood and softwood fibers were isolated. The fiber mat from the feed liquor soap also contained some calcium sulfate crystals.

4 SUMMARY AND CONCLUSIONS

When this work was commenced, it was reasonable to expect (Niemelä 2003, Räsänen 2003) that:

- Sulfate soaps may contain high amounts (more than 30 g/kg) of fibers.
- The amount and nature of the fibers depend on the pulping process and raw materials used at the mill.
- More detailed characterization of the fibers and other solid materials (dirt) in soap would help to understand their origins and detrimental roles in the soap separation (and soap quality).
- Sampling of the soaps at different soap separation points would clarify the main inputs of the fibers and other impurities.

Therefore, a lot of attention was now paid to the isolation of the fibers and dirt from the soaps, and for the careful controlling that no artifacts and "normal" soap components interfere with the desired fractions. This resulted in the procedure where the isolated materials are washed with some acetone, to dissolve possibly present tall oil residues. It was also found that the sulfuric acid acidulations of soap always produce varying amounts of calcium sulfate crystals that need to be washed with hydrochloric acid. If this step is omitted, too high figures for the fibers + dirt are recorded. It was also found essential to study the fiber fractions under microscope for their more detailed characterization. In this work, a large number of photographs were taken.

Using the described washing steps and hydrochloric or sulfuric acid acidulation, fibers and dirt were isolated from all the investigated soap samples but their concentrations were constantly lower than expected or usually reported before. The most typical concentrations were in the range of 1-3 g/kg. That usually also contained material other than just fibers.

Although not known with 100% certainty, it is reasonable to expect that the previously reported high fiber contents in the soaps have been caused by material other than just fibers. That may also include calcium sulfate crystals formed during acidulation, tall oil residues that should be washed with an organic solvent, and other materials. There is even a risk of unreacted soap after acidulation, particularly if there are elevated amounts of calcium fatty acid salts present.

The current comparison of the fiber + dirt fractions isolated from different soaps (different mills, different soap separation points) did not reveal as distinct differences between the mills or cooking processes as perhaps expected.

Altogether, the current findings on the amounts and nature of the fibers and dirt in the soap samples made it necessary to reconsider the objectives and analytical tasks of the whole work. Some attention was paid to the characterization of the dirt fraction, which indicated varying amounts of lignin, unreacted soap, defoamers, metal salts or precipitates, agglomerates of neutral extractives, and other materials. They were found both after sulfuric acid and hydrochloric acid acidulation, but are still only partially characterized. In many cases, however, clean fiber fractions with little or no dirt were isolated.

No clear correlations between the fibers, other soap impurities, and various process conditions are evident. The soaps from all the mills and soap separation points contained non-process elements in varying amounts, lignin and other organic impurities, and fibers. One of the main obstacles is that in many cases it is impossible to determine the true content of the fibers as there are different dirt matrices present. On the other hand, it hardly makes sense to compare fiber + dirt fractions with pure fiber fractions, frequently isolated. Thus, the whole question becomes much more complex than expected.

The compositions of the tall oil compounds in the soaps were also determined, making it possible to separate pure softwood oils from mixed oils. As the tall oils also have different compositions, there remains a possibility that these compositions also affect soap separation and interference with various impurities. This is another complex question that can hardly be answered at the moment.

In this work, a number of novel methods were also developed and applied for the analysis of various soap impurities. These include detailed GC/MS method for turpentine and polar carboxylic acids, and laser ablation for the distribution of the non-process elements. As a result, a useful and comprehensive package of analytical methods is now available for the studies on soap separation and quality. In a separate report, Sirén (2007) describes the development and potential of other new methods used to study the soap separation rates.

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APPENDICES

- Appendix 1: Composition of the soap samples from the mills (4 pages).
- Appendix 2: Group composition of the crude tall oils from the acidulation of the soap samples (1 page).
- Appendix 3: Detailed compositions of the crude tall oils from the acidulation of the soap samples (5 pages).
- Appendix 4: Examples of non-process elements determination on the frozen surface of selected soap samples (5 pages).
- Appendix 5: Photos of fibers and other solid impurities ("dirt") isolated from different soap samples (12 pages).
- Appendix 6: Mill data on soap separation and handling (5 pages).

Appendix 1a. Composition of the soap samples from the Botnia and UPM mills. The non-process elements (NPEs) are given in App. 1b. –, not analyzed.

Mill Soap sampling point	Dry sols.	Tall oil	Na	K	NPEs	Tur- pent.	Lig- nin	Polar acids	Fiber
	%	%	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg
<i>Joutseno</i>									
Weak liquor	65.8	52	44	3.9	2.7	7.9	9	11	4.1
Intermediate liquor	52	–	50	4.6	1.5	–	–	–	–
Acidulation feed	58.3	51.5	41	3.7	2.1	6.5	7	14	0.9
<i>Kaskinen</i>									
Feed liquor (birch)	64.3	–	37	4	3.3	–	–	–	–
Interm. liquor (birch)	68.1	–	44	4.7	2.9	–	–	–	1.9
Acidul. feed (birch)	59.7	53.6	33	3.6	2.5	0.1	9	13	4.9
Acidul. feed (aspen)	58.8	44.7	36	3.5	2.2	–	–	18	–
<i>Kemi</i>									
Feed liquor	51.5	–	46	2	1.1	7.4	–	–	–
Collection tank	57.7	–	44	1.9	1.2	–	–	–	–
Acidulation feed	58.9	54.2	40	1.7	1.3	6.6	8	11	2.2
<i>Rauma</i>									
Collection tank	57.8	–	43	3.8	2.6	–	–	–	1.6
Acidulation feed	61.3	58	43	3.8	3.5	10.6	5	12	2.2
<i>Äänekoski</i>									
Acidulation feed	59.4	55.7	36	2.7	2.5	4.1	4	17	0.7
<i>Kaukas</i>									
Chemical plant	60.2	–	42	3.2	3.1	9.7	–	–	2.7
Acidulation feed	62.1	57.4	38	2.9	3	8.7	5	–	2.4
<i>Kymi</i>									
Feed liquor 1	65.9	–	39	4.3	1.3	1.1	–	–	–
Feed liquor 2	60	–	38	4.2	4.3	4.5	–	–	2
Intermediate liquor 1	64.9	55.5	39	4.4	1.8	–	10	6	2
Intermediate liquor 2	71.1	–	48	5.3	2.1	0.9	–	–	6.7
Acidulation feed	60.2	47.3	39	4.4	2.3	5.5	11	9	0.3
<i>Pietarsaari</i>									
Collection tank	60.5	–	39	2.7	2.6	7.4	–	–	–
Storage tank	60.2	–	39	2.7	2.6	–	–	–	–
Acidulation feed	59.6	55.1	38	2.7	2.4	6	5	15	3.6
<i>Tervasaari</i>									
SAP soap	50.5	–	37	1.1	2.3	0.2	–	–	4.3
Kraft weak liquor	55.3	–	45	1.5	1.4	–	–	–	1.7
Intermediate liquor	39.9	–	31	1	2.1	0.4	–	–	–
Acidulation feed	53.2	44.7	39	1.2	1	0.4	9	14	?*

*Recorded value 25.7 probably too high (unreacted soap present?).

Appendix 1b. The non-process elements in the soap samples from the Botnia and UPM mills. The figures are given as mg/kg soap. D., distribution analysed by laser ablation.

Mill Soap sampling point	Ca	Mg	Si	Mn	Fe	Al	Zn	P	D.
<i>Joutseno</i>									
Weak liquor	1700	520	270	100	20	59	26	180	
Intermediate liquor	700	390	310	49	19	51	9	78	
Acidulation feed	1300	480	200	83	13	42	19	210	X
<i>Kaskinen</i>									
Feed liquor (birch)	1500	1200	320	140	17	46	92	290	
Interm. liquor (birch)	1200	1100	360	120	23	45	93	300	
Acidul. feed (birch)	1200	860	240	110	13	33	72	250	X
Acidul. feed (aspen)	900	840	260	98	31	31	74	210	
<i>Kemi</i>									
Feed liquor	640	120	150	63	120	20	29	55	X
Collection tank	810	73	200	73	5	19	37	68	
Acidulation feed	870	100	160	72	53	17	35	67	
<i>Rauma</i>									
Collection tank	2000	280	130	69	7	27	45	160	
Acidulation feed	2900	300	140	85	8	28	55	190	X
<i>Äänekoski</i>									
Acidulation feed	1700	470	96	150	15	23	69	210	X
<i>Kaukas</i>									
Chemical plant	1700	1100	120	96	50	23	38	270	
Acidulation feed	2300	450	120	91	14	23	45	260	X
<i>Kymi</i>									
Feed liquor 1	880	170	69	85	53	12	31	110	
Feed liquor 2	1700	1800	300	330	12	38	84	280	
Intermediate liquor 1	1000	470	130	110	20	20	35	140	
Intermediate liquor 2	1200	520	160	140	8	22	46	170	
Acidulation feed	1000	910	180	170	8	24	44	150	X
<i>Pietarsaari</i>									
Collection tank	1700	590	120	76	6	32	35	220	
Storage tank	1700	600	120	77	7	28	37	220	
Acidulation feed	1600	520	100	68	6	27	33	200	X
<i>Tervasaari</i>									
SAP soap	1500	220	400	53	49	24	4	340	
Kraft weak liquor	1100	34	110	64	24	27	22	140	X
Intermediate liquor	1800	61	120	78	31	23	23	180	
Acidulation feed	790	54	120	35	8	12	10	120	

Appendix 1c. Composition of the soap samples from the Sunila and Stora Enso mills.
The non-process elements (NPEs) are given in App. 1d. –, not analyzed.

Mill Soap sampling point	Dry sols.	Tall oil	Na	K	NPEs	Tur- pent.	Lig- nin	Polar acids	Fiber
	%	%	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg
<i>Sunila</i>									
Collection tank 1	62.8	–	45	3	3.2	3	–	–	–
Collection tank 2	55.1	–	43	2.9	2.0	–	–	–	–
Handling tank 1	62.2	–	44	3	3.3	–	–	–	–
Handling tank 2	62.2	–	44	2.9	3.5	–	–	–	–
Acidulation feed	62	47.9	45	3	3.1	3	9	16	2.6
<i>Enocell</i>									
Feed liquor 1	61.6	48.2	35	4	2.4	1.5	7	19	2.5
Feed liquor 2	67.7	–	35	4.3	2.9	–	–	–	–
Intermediate liquor	65.5	–	45	4.7	5.1	0.1	–	–	2.5
Acidulation feed	61.7	49.7	36	4	2.2	1.7	9	15	1.5
<i>Imatra</i>									
Storage tank 1	66	–	44	4.5	2	–	–	–	–
Storage tank 2	66.3	–	43	4.4	1.8	2.2	–	–	–
Acidulation feed 1	65.3	54.9	44	4.6	2	–	11	13	–
Acidulation feed 2	61.7	61.1	41	4.3	1.9	0.9	7	14	0.9
<i>Kemijärvi</i>									
Wash liquor	68.3	–	41	2.7	1.6	18.6	–	–	–
Feed liquor	–	–	58	3.6	2.4	9.5	–	–	–
Intermediate liquor	74.6	–	54	3.6	2	0.2	–	–	2
Acidulation feed	–	61.6	35	2.2	1.8	19.6	10	17	2.3
<i>Kotka</i>									
Feed liquor	65.7	–	37	3.2	6.6	1.5	–	–	3.5
Intermediate liquor	67.8	–	47	3.8	2.1	–	–	–	3
Acidulation feed	66.1	57.8	40	3.5	7.4	2.2	8	12	0.6
<i>Oulu</i>									
Acidulation feed	61.5	53.8	38	2.4	2.7	7.2	9	16	1.3
<i>Varkaus</i>									
Feed liquor 1	64.8	–	40	2.4	2.4	–	–	–	–
Feed liquor 2	63	–	41	2.5	2.4	2.2	–	–	1.9
Intermediate liquor	51	–	50	3.2	1.8	–	–	–	8
Acidulation feed	64.7	56.7	44	2.6	2.4	1.5	8	11	2.4
<i>Veitsiluoto</i>									
Wash liquor	44.3	–	28	1.6	0.7	–	–	–	–
Feed liquor 1	63.7	–	39	2.1	2.2	3	–	–	3.2
Feed liquor 2	57.3	–	39	2.2	3.6	–	–	–	–
Intermediate liquor 1	66.8	–	46	2.4	2	–	–	–	1.2
Intermediate liquor 2	66.1	–	44	2.5	2.6	–	–	–	–
Acidulation feed	57.4	54.3	35	1.9	1.7	1.9	6	14	0.5

Appendix 1d. The non-process elements in the soap samples from the Sunila and Stora Enso mills. The figures are given as mg/kg soap. Distr., distribution analysed by laser ablation.

Mill Soap sampling point	Ca	Mg	Si	Mn	Fe	Al	Zn	P	D.
<i>Sunila</i>									
Collection tank 1	2500	400	180	63	30	50	17	270	X
Collection tank 2	1500	300	130	41	7	27	9	130	
Handling tank 1	2600	420	160	65	11	42	17	270	
Handling tank 2	2800	380	180	64	10	44	33	280	
Acidulation feed	2400	380	160	61	23	39	17	250	X
<i>Enocell</i>									
Feed liquor 1	1900	95	220	94	11	19	53	180	X
Feed liquor 2	1900	320	320	170	35	28	90	200	
Intermediate liquor	2500	1100	730	430	13	61	270	280	
Acidulation feed	1700	68	210	89	30	18	49	160	
<i>Imatra</i>									
Storage tank 1	1400	150	93	230	6	20	110	310	
Storage tank 2	1100	210	120	240	12	22	130	250	
Acidulation feed 1	1400	150	92	230	8	21	110	290	
Acidulation feed 2	1100	210	110	250	34	25	130	230	
<i>Kemijärvi</i>									
Wash liquor	990	350	94	150	5	14	36	99	
Feed liquor	1500	370	120	250	17	32	100	180	
Intermediate liquor	1200	350	150	180	10	20	62	160	
Acidulation feed	1100	380	120	150	3	15	31	95	X
<i>Kotka</i>									
Feed liquor	5700	160	440	120	98	38	45	320	
Intermediate liquor	1400	240	290	69	52	33	30	170	
Acidulation feed	6500	200	440	140	43	54	46	340	X
<i>Oulu</i>									
Acidulation feed	1800	570	120	140	7	25	53	410	X
<i>Varkaus</i>									
Feed liquor 1	1600	390	180	120	4	36	58	350	
Feed liquor 2	1700	390	150	120	4	22	58	360	
Intermediate liquor	1000	400	180	110	4	19	52	230	
Acidulation feed	1600	380	200	110	41	24	60	590	X
<i>Veitsiluoto</i>									
Wash liquor	1500	450	75	98	14	21	37	350	
Feed liquor 1	2700	480	100	160	32	25	70	530	X
Feed liquor 2	1200	270	62	90	300	15	35	280	
Intermediate liquor 1	1500	740	120	150	16	28	52	330	
Intermediate liquor 2	1300	220	50	84	9	14	34	320	
Acidulation feed	1500	450	75	98	14	21	37	350	X

Appendix 2. Composition (%) of the crude tall oils from the acidulation of the soap samples. "Separated oil" refers to the oil separated spontaneously (top layer) after the acidulation, and "total oil" refers to ether extract of the entire acidulation mixture (including the spontaneously separated oil and the oil in the lignin phase).

Mill, soap sampling point*	Spontaneosuly separated oil				Total oil			
	Fatty acids	Resin acids	Suberin acids	Neutral comps.	Fatty acids	Resin acids	Suberin acids	Neutral comps.
Joutseno, WL	54.6	36.7	0.2	8.8	53.4	36.2	0.2	10
Joutseno, AF	54.9	37.1	0.3	8.2	54.5	35.2	0.3	9.3
Kaskinen, AFb	53.7	16.7	0.4	28.6	56	17.5	0.5	25.6
Kaskinen, AFa	53.6	16.2	0.3	29.5	54.9	15.9	0.2	28.6
Kemi, AF	52.1	32.1	0.6	14.6	51.4	32.9	0.6	15.2
Rauma, AF	53.3	38.1	0.3	8.3	54.4	36.7	0.2	8.7
Äänekoski, AF	58.6	24.7	0.2	16.5	55.5	24.9	0.4	18.7
Kaukas, AF	55.2	27.5	0.2	17.1	54.5	28.6	0.2	16.4
Kymi, AF	53.4	27.9	0.8	17.1	49.7	28.5	1.1	19.4
Pietarsaari, AF	54.7	29.3	0.3	14.9	53.9	28.7	0.4	16.1
Tervasaari, AF	56.8	34.1	0	9	56	34.9	0	8.9
Sunila, AF	49.7	40.9	0.3	9.3	49.8	39.5	0.2	9.1
Enocell, FL 1	52.7	24.2	0.3	21.7	52.4	23.4	0.2	22.9
Enocell, AF	52.3	23.4	0.4	22.9	49.5	24.1	0.5	25.8
Imatra, AF 1	49.5	33.6	0.2	15.8	47.6	34.9	0.2	16.5
Imatra, AF 2	48.7	26.9	0.3	22.7	48.2	26.4	0.2	25.3
Kemijärvi, AF	47.6	39.3	0.4	12.5	47.5	38.7	0.3	12
Kotka, AF	52.1	37.2	0.3	9.8	–	–	–	–
Oulu, AF	53	31.1	0.2	16.4	50.6	33.3	0.3	15
Varkaus, AF	52.5	28.6	0.2	17.8	49.2	27.9	0.3	21.8
Veitsiluoto, AF	–	–	–	–	51.6	28.2	0.3	19.8

*WL, weak liquor; AF, acidulation feed; AFb, acidulation feed birch cooking; AFa, acidulation feed aspen cooking; FL, feed liquor.

Appendix 3. Composition (%) of the spontaneously separated (S) and total (T) tall oils; cf. Appendix 2.

Main group Compound	Jouts. WL		Jouts. AF		Kask. AFa		Kask. AFb	
	S	T	S	T	S	T	S	T
Fatty acids	54.6	53.4	54.9	54.5	53.6	54.9	53.7	56
Myristic acid	0.1	0.1	0.1	0.1	0.3	0.3	0.3	0.2
Methylmyristic acid	0.3	0.3	0.1	0.2	0.3	0.3	0.3	0.2
Palmitic acid	1.4	1.6	1.5	1.6	5	5.3	4.9	5.2
Methylpalmitic acid	1.2	1.3	1.3	1.3	0.9	0.8	0.4	0.3
Heptadecanoic acid	0.3	0.2	0.2	0.2	0.3	0.2	0.3	0.3
Stearic acid	1.5	2	0.8	1.1	3.3	3.5	3.5	3.5
Eicosanoic acid	0.2	0.2	0.2	0.1	2.3	2.1	2.7	2.4
Docosanoic acid	0.9	0.9	0.7	0.8	2.8	2.5	3.3	2.6
Tricosanoic acid	0.2	0.2	0.1	0.2	0.6	0.5	0.7	0.8
Tetracosanoic acid	0.7	0.5	0.4	0.5	0.8	0.7	1.3	1.6
Palmitoleic acids (2)	0.5	0.8	0.9	0.9	0.9	0.9	0.5	0.6
Oleic acid	7.1	6.8	11.4	9.1	5.4	6.5	4.6	5.3
Elaidic acid	1.1	1.2	0.8	1.2	0.7	0.8	0.8	0.9
Linoleic acid	20.2	18.4	18.9	17.8	24	23.9	22	25.1
Linoleic acid isomer 1	2.5	2.4	1.4	1.6	2.2	2.4	1.7	2.1
Linoleic acid isomer 2	2.8	2.4	2.8	3	1	1.1	1.8	0.8
Linoleic acid isomer 3	1.1	1.1	0.6	1	0.6	0.7	0.9	0.6
Linoleic acid isomer 4	2.2	2.3	2.4	2.9	1.2	1.5	2.5	2.5
Linolenic acid	8	8.5	8.8	8.8	0.7	0.8	0.7	0.7
Linolenic acid isomer	2.3	2.2	1.5	2.1	0.3	0.1	0.5	0.3
Suberin acids	0.2	0.2	0.3	0.3	0.3	0.2	0.4	0.5
Resin acids	36.7	36.2	37.1	35.2	16.2	15.9	16.7	17.5
Pimaric acid	2.3	4	3.3	3.5	1.1	1.2	0.9	0.4
Sandaracopimaric acid	1.1	1.2	1	1.1	0.7	0.6	0.7	0.9
Isopimaric acid	2.8	3.1	2.5	2.5	1.1	1	1	1.1
Palustric + levopimaric acids	1.5	1.6	1.8	1.2	1	0.9	1.3	1.2
Abietic acid	17.9	16.6	19.6	17.4	7.5	7.6	7.7	8.5
Neoabietic acid	1.3	1	1.3	1	0.4	0.3	0.4	0.3
Dehydroabietic acid	9.3	8	7.1	8	3.9	3.9	4.3	4.6
Oxidised resin acids	0.5	0.7	0.5	0.5	0.5	0.4	0.4	0.5
Neutral compounds	8.8	10	8.2	9.3	29.5	28.6	28.6	25.6
1-Docosanol	0.1	0.2	0.1	0.1	0.1	0.1	0.2	0.2
1-Tetracosanol	0.1	0.2	0.1	0.2	0.1	0.1	0.2	0.1
Neutral diterpenes	1.1	1.2	0.9	0.8	0.2	0.1	0.3	0.3
Campesterol	0.9	0.9	0.9	1.1	1.1	1.1	0.6	1
β -Sitosterol	4.2	4.5	4.7	5.2	6	5.9	6.6	6.3
β -Sitostanol	0.6	0.7	0.7	0.8	1	1.8	1.8	1.6
Cycloartanol	0.5	0.5	0.4	0.5	1.4	1.4	1.4	1.1
24-Methylenecycloartanol	0.4	0.5	0.4	0.4	3.2	3.2	3	2.4
Lupeol					0.9	1	1.6	1.3
Citrostadienol	0.3	0.2			3.8	3.3	3.8	3
Betulinol + methyl betulinate					3.8	2.5	3.1	2.4
Squalene	0.6	1.1			3.4	3.7	2.3	2.5
Betulaprenols				0.2	4.5	4.4	3.7	3.4

Appendix 3 (cont.). Composition (%) of the spontaneously separated (S) and total (T) tall oils; cf. Appendix 2.

Main group Compound	Kemi AF		Rauma AF		Ä-koski AF		Kaukas AF	
	S	T	S	T	S	T	S	T
Fatty acids	52.1	51.4	53.3	54.4	58.6	55.5	55.2	54.5
Myristic acid	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.1
Methylmyristic acid	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.3
Palmitic acid	2.4	2.3	1.2	1.5	3.4	3.4	2.7	2.8
Methylpalmitic acid	0.8	0.8	1	1.1	0.7	0.8	0.9	1
Heptadecanoic acid	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.2
Stearic acid	1.8	1.1	1	1.1	1.7	1.8	1.3	1.5
Eicosanoic acid	1	1.1	0.5	0.3	1.1	1.3	0.9	1
Docosanoic acid	1.4	1.6	0.9	1.1	1.5	1.7	1.5	1.6
Tricosanoic acid	0.2	0.1	0.2	0.2	0.3	0.3	0.2	0.3
Tetracosanoic acid	0.6	0.6	0.5	0.3	0.5	0.6	0.6	0.7
Palmitoleic acids (2)	0.5	0.6	0.6	0.5	0.5	0.6	0.7	0.8
Oleic acid	8.2	7.8	7.1	8.5	10.7	8.8	10	8.8
Elaidic acid	1.1	1.4	1	1.1	1.1	1.2	1.3	1.2
Linoleic acid	19.2	18.1	18	17.1	22.8	20.6	17.7	16.4
Linoleic acid isomer 1	1.6	1.6	3.4	3.5	2.4	2.3	2.4	2.6
Linoleic acid isomer 2	2.3	2.5	3.5	3.5	2	2.2	3.4	3.1
Linoleic acid isomer 3	0.4	0.4	1.2	1.1	0.6	0.6	1	0.9
Linoleic acid isomer 4	2.2	2.3	2.4	2.3	1.5	1.5	3.8	3.9
Linolenic acid	6.8	6.8	7	7.2	5.6	5.6	4.5	5.4
Linolenic acid isomer	1.1	1.8	3.4	3.6	1.6	1.6	1.9	1.9
Suberin acids	0.4	0.6	0.3	0.2	0.2	0.4	0.2	0.2
Resin acids	32.1	32.9	38.1	36.7	24.7	24.9	27.5	28.6
Pimaric acid	3.4	3.2	3	4	2.7	2.7	2	2.1
Sandaracopimaric acid	0.8	0.9	0.9	1	0.6	0.7	0.8	0.9
Isopimaric acid	2.5	2.4	2.8	2.6	1.5	1.5	2.2	2.2
Palustric + levopimaric acids	1.4	1.5	1.9	1.6	0.3	1.1	0.4	1.5
Abietic acid	16.1	16.3	18.8	18.1	12.8	12	14.1	13.4
Neoabietic acid	0.9	1.3	1.3	1.1	0.5	0.7	0.6	1
Dehydroabietic acid	6.6	6.9	8.8	7.9	5.8	5.8	7	7.2
Oxidised resin acids	0.4	0.4	0.6	0.4	0.5	0.4	0.4	0.3
Neutral compounds	14.6	15.2	8.3	8.7	16.5	18.7	17.1	16.4
1-Docosanol	0.2	0.1	0.1	0.1				
1-Tetracosanol	0.1	0.1	0.1	0.1				
Neutral diterpenes	0.8	0.9	1.3	0.9	0.5	0.6	0.8	0.8
Campesterol	0.5	0.6	0.8	0.9	0.4	0.4	1	1
β-Sitosterol	5.1	5.2	4.5	5.1	5.5	5.7	6.6	6.1
β-Sitostanol	1.1	1.3	0.7	0.8	1.2	1.4	1.1	1.1
Cycloartanol	0.8	0.9	0.5	0.4	0.9	1	1	0.9
24-Methylenecycloartanol	1.2	1.2	0.3	0.4	1.4	1.5	1.2	1.3
Lupeol	0.5	0.5			0.3	0.5		0.2
Citrostadienol	1.1	1.2			1.8	2	1.6	1.6
Betulinol + methyl betulinate	1.2	1.5			1.4	1.8	1	1.1
Squalene	0.6	0.6			1.6	1.7	1	1
Betulaprenols	1.4	1.1			1.5	2.1	1.8	1.3

Appendix 3 (cont.). Composition (%) of the spontaneously separated (S) and total (T) tall oils; cf. Appendix 2.

Main group Compound	Kymi AF		P-saari AF		T-saari AF		Sunila AF	
	S	T	S	T	S	T	S	T
Fatty acids	53.4	49.7	54.7	53.9	56.8	56	49.7	49.8
Myristic acid	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1
Methylmyristic acid	0.3	0.3	0.2	0.2	0.2	0.2	0.3	0.3
Palmitic acid	2.6	2.5	2.7	2.6	1.8	1.8	1.3	1.5
Methylpalmitic acid	1	1	0.9	0.8	1.4	1.3	1.2	1.3
Heptadecanoic acid	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.2
Stearic acid	1.9	2.2	1.5	1.1	1.3	1.1	1.4	1.4
Eicosanoic acid	1.2	1.2	0.9	0.9	0.4	0.3	0.3	0.4
Docosanoic acid	1.5	1.6	1.3	1.3	0.8	0.8	1	1
Tricosanoic acid	0.5	0.3	0.2	0.2	0.1	0.1	0.3	0.3
Tetracosanoic acid	0.6	0.7	0.5	0.5	0.5	0.5	0.8	0.7
Palmitoleic acids (2)	0.7	0.4	0.6	0.5	0.6	0.7	0.7	0.6
Oleic acid	6.2	5.8	9.4	9.7	9.5	10.3	8.5	7.9
Elaidic acid	1.1	0.9	0.9	1.3	1.1	1	1	1.2
Linoleic acid	18.7	16.9	20	18.8	21.2	19	15.7	15.4
Linoleic acid isomer 1	2.9	2.3	1.9	1.8	1.4	1.5	1.8	2
Linoleic acid isomer 2	2.6	2.7	2	2.7	1.8	2.6	1.8	1.6
Linoleic acid isomer 3	0.9	1	0.7	0.6	0.8	1	2.1	1.8
Linoleic acid isomer 4	3.1	2.9	2.8	2.7	3.2	3.1	3	2.8
Linolenic acid	6.5	5.9	6.3	6	9.7	9.3	6.6	7.1
Linolenic acid isomer	0.8	0.7	1.6	1.9	0.7	0.9	1.5	2.2
Suberin acids	0.8	1.1	0.3	0.4			0.3	0.2
Resin acids	27.9	28.5	29.3	28.7	34.1	34.9	40.9	39.5
Pimaric acid	2.2	2.1	2.6	2.7	2.7	3.4	3.1	3.3
Sandaracopimaric acid	0.9	1	0.7	0.7	1.2	1.2	1.2	1.3
Isopimaric acid	2.4	2.5	2.1	1.9	3.1	3	3	3
Palustric + levopimaric acids	1.3	1.6	1.3	1.5	1.2	1.6	1.7	1.4
Abietic acid	13.7	13	14.6	14.5	17.6	17.2	19.5	18.3
Neoabietic acid	0.8	1.1	0.8	1.1	1.1	1.3	1.3	1.2
Dehydroabietic acid	6	6.5	6.7	5.7	6.7	6.9	10.4	10.1
Oxidised resin acids	0.6	0.7	0.5	0.6	0.5	0.3	0.7	0.9
Neutral compounds	17.1	19.4	14.9	16.1	9	8.9	9.3	9.1
1-Docosanol	0.2	0.3	0.1	0.1	0.2		0.2	0.2
1-Tetracosanol	0.3	0.3	0.1	0.1	0.2		0.2	0.2
Neutral diterpenes	1.2	1.4	0.6	0.6	1.6	1.4	0.7	0.5
Campesterol	0.7	0.8	0.5	0.6	1	1	1	0.8
β -Sitosterol	4.9	5.3	5.5	5.8	4.7	5	4.8	4.7
β -Sitostanol	1.2	1.3	1.3	1.4	0.8	0.7	0.9	0.7
Cycloartanol	0.9	1.1	0.8	0.9	0.4	0.4	0.4	0.5
24-Methylenecycloartanol	1.3	1.5	1.1	1.2	0.3	0.4	0.4	0.5
Lupeol	0.4	0.5	0.4	0.5				
Citrostadienol	1.4	1.6	1.1	1.3				0.2
Betulinol + methyl betulinate	1.4	1.8	1.3	1.5				
Squalene	1.3	1.4	0.9	0.9				
Betulaprenols	1.9	2.1	1.2	1.2			0.7	0.8

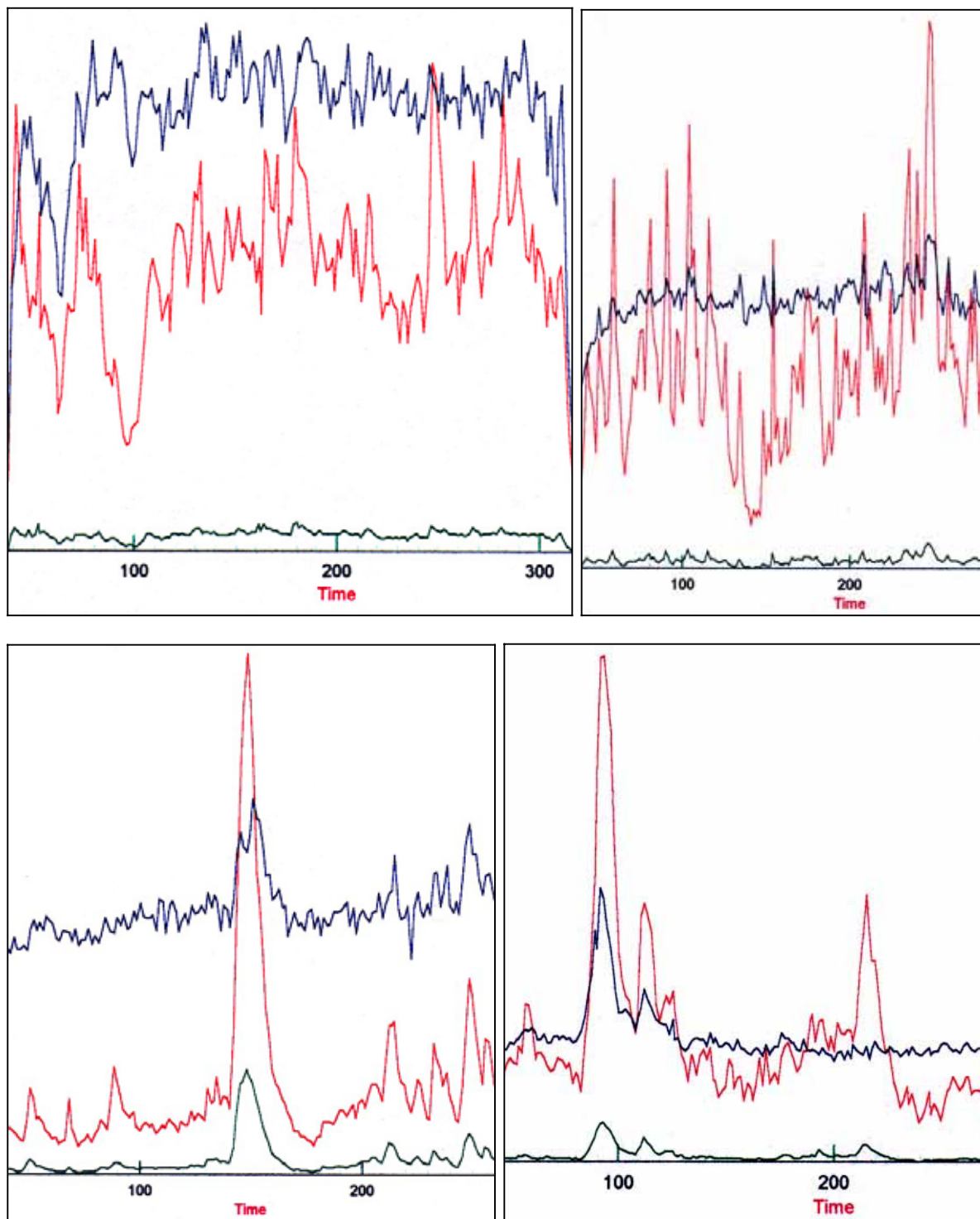
Appendix 3 (cont.). Composition (%) of the spontaneously separated (S) and total (T) tall oils; cf. Appendix 2.

Main group Compound	Enocell FL 1		Enocell AF		Imatra AF1		Imatra AF2	
	S	T	S	T	S	T	S	T
Fatty acids	52.7	52.4	52.3	49.5	49.5	47.6	48.7	48.2
Myristic acid	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.2
Methylmyristic acid	0.3	0.3	0.3	0.2	0.2	0.2	0.3	0.2
Palmitic acid	3.8	3.4	3.3	3.3	2.3	2.3	3.4	3.4
Methylpalmitic acid	0.8	0.7	0.7	0.7	0.6	0.5	0.5	0.5
Heptadecanoic acid	0.2	0.2	0.3	0.3	0.2	0.2	0.2	0.2
Stearic acid	2.2	2.4	2.7	1.9	1.8	1.2	2.7	2.2
Eicosanoic acid	2	2.1	2	1.9	1.1	1	1.9	1.8
Docosanoic acid	2.5	2.7	2.2	2.4	1.5	1.4	2.3	2.4
Tricosanoic acid	0.8	0.6	0.7	0.6	0.2	0.2	0.7	0.4
Tetracosanoic acid	0.9	1.1	0.7	0.8	0.5	0.4	0.8	0.9
Palmitoleic acids (2)	0.9	0.8	0.6	0.5	0.5	0.4	0.6	0.6
Oleic acid	5.3	4.1	5.5	5.2	6.9	7.8	4.6	5.1
Elaidic acid	0.9	0.8	0.9	0.9	1.2	1.1	0.7	0.8
Linoleic acid	18	17.7	18.3	16.8	19.2	18.1	19.4	18.4
Linoleic acid isomer 1	2.4	3.3	2.3	2.5	1.6	1.6	2.3	2.3
Linoleic acid isomer 2	3	2.3	2.8	3	1.9	1.8	1.3	1.3
Linoleic acid isomer 3	0.9	1.9	0.9	0.8	0.7	0.6	0.5	0.6
Linoleic acid isomer 4	3.8	3.6	3.3	3	2	1.7	2	1.9
Linolenic acid	2.7	2.9	3.4	3.1	5.9	5.8	3.7	3.6
Linolenic acid isomer	1.1	1.3	1.2	1.4	1.1	1.2	0.6	1.4
Suberin acids	0.3	0.2	0.4	0.5	0.2	0.2	0.3	0.2
Resin acids	24.2	23.4	23.4	24.1	33.6	34.9	26.9	26.4
Pimaric acid	2.3	2.6	1.8	2.4	3.5	3.5	2	2.2
Sandaracopimaric acid	0.9	0.9	0.8	0.8	0.9	0.9	0.8	0.8
Isopimaric acid	1.8	2	2	2	2.4	2.3	1.9	1.8
Palustric + levopimaric acids	1.2	1.1	1.3	1.4	1.6	2.1	1.6	1.7
Abietic acid	11	9.8	10.6	10.6	17.1	17.6	13.5	12.7
Neoabietic acid	0.5	0.5	0.6	0.9	1	1.5	0.8	1
Dehydroabietic acid	6	5.9	5.7	5.5	6.6	6.7	5.8	5.9
Oxidised resin acids	0.5	0.6	0.6	0.5	0.5	0.3	0.5	0.3
Neutral compounds	21.7	22.9	22.9	25.8	15.8	16.5	22.7	25.3
1-Docosanol				0.1	0.1	0.2		
1-Tetracosanol	0.1	0.1		0.1	0.2	0.2		
Neutral diterpenes	0.5	0.3	0.4	0.4	0.6	0.5	0.2	0.6
Campesterol	0.7	0.6	0.5	0.7	0.3	0.3	0.2	1.1
β -Sitosterol	5.1	5.2	5.3	6.1	5.1	5.3	6.1	6.2
β -Sitostanol	1.2	1.3	1.3	1.6	1.1	1.2	1.6	1.6
Cycloartanol	1.2	1.4	1.4	1.7	0.9	1	1.3	1.5
24-Methylenecycloartanol	2.1	2.3	2.3	2.6	1.2	1.2	2.2	2.4
Lupeol	1	0.9	0.5	0.5	0.4	0.3	0.8	0.8
Citrostadienol	2.4	2.6	2.7	3.2	1.6	1.6	3.3	3.2
Betulinol + methyl betulinate	1.5	1.8	1.6	1.9	1.1	1.3	1.4	2.5
Squalene	1.7	1.9	2.6	2.8	1.4	1.3	2.1	2.1
Betulaprenols	4.2	4.5	4.3	4.1	1.8	2.1	3.5	3.3

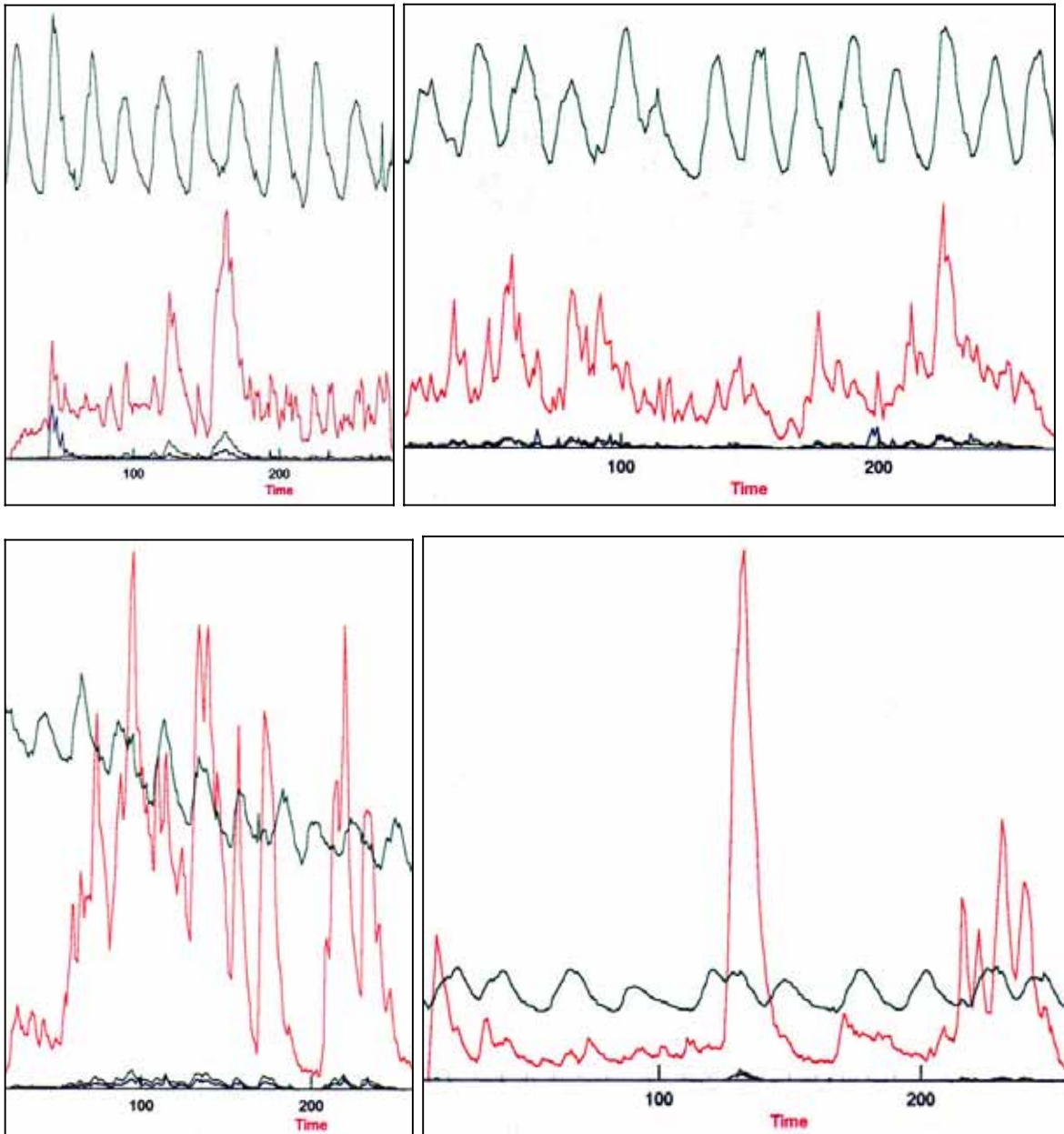
Appendix 3 (cont.). Composition (%) of the spontaneously sperated (S) and total (T) tall oils; cf. Appendix 2. Kot., Kotka; Veit., Veitsiluoto.

Main group Compound	Kemij. AF		Kot.	Oulu AF		Varkaus AF		Veit.
	S	T	S	S	T	S	T	T
Fatty acids	47.6	47.5	52.1	53	50.6	52.5	49.2	51.6
Myristic acid	0.1	0.1		0.2	0.2	0.1	0.1	0.1
Methylmyristic acid	0.2	0.2		0.2	0.2	0.2	0.2	0.1
Palmitic acid	1	1.1	1.4	2.7	2.5	3.3	3.3	2.6
Methylpalmitic acid	0.9	1.1	0.8	0.6	0.4	0.7	0.6	0.5
Heptadecanoic acid	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.1
Stearic acid	1	1	1	1.5	1.4	1.9	1.6	1.6
Eicosanoic acid	0.4	0.1	0.4	1.2	1.1	1.7	1.6	1.1
Docosanoic acid	1	1	0.7	1.7	1.7	2.1	2.2	1.4
Tricosanoic acid	0.4	0.3	0.2	0.3	0.4	0.7	0.4	0.1
Tetracosanoic acid	0.7	0.6	0.5	0.8	0.6	0.8	0.8	0.3
Palmitoleic acids (2)	0.8	0.7	0.2	0.6	0.6	0.5	0.5	0.3
Oleic acid	5.7	8.2	10.2	9.1	8.8	6.5	7.7	9.8
Elaidic acid	0.9	0.7	1.3	1.1	1	0.7	0.8	1.3
Linoleic acid	16.1	15.3	12.9	17.1	17.7	20.7	18.5	20
Linoleic acid isomer 1	3.1	3.1	4.9	2.6	2.1	2.4	1.8	1.8
Linoleic acid isomer 2	3	3	4.8	2.6	2.4	1.4	1.4	1.8
Linoleic acid isomer 3	0.9	1.3	0.9	0.8	0.7	0.7	0.5	0.3
Linoleic acid isomer 4	1.5	1.1	1.5	2.3	2.2	3	2.7	1.3
Linolenic acid	7.1	7.8	4.5	5.9	5.5	4	3.1	5.5
Linolenic acid isomer	2.6	0.7	5.7	1.5	0.9	0.9	1.2	1.6
Suberin acids	0.4	0.3	0.2	0.2	0.3	0.2	0.3	0.3
Resin acids	39.3	38.7	37.2	31.1	33.3	28.6	27.9	28.2
Pimaric acid	3.5	5.4	3.4	3.1	3.3	2.3	2	3.1
Sandaracopimaric acid	1	1	1	0.9	0.9	0.8	0.5	0.6
Isopimaric acid	3.6	3.3	2.8	2.3	2.3	2	1.7	1.9
Palustric + levopimaric acids	1.9	1.6	2.2	1	1.4	1.6	1.7	1.2
Abietic acid	17.5	16.7	15.8	14.3	15.4	14.2	14	13.9
Neoabietic acid	1.1	0.9	3.4	0.6	0.7	0.7	1	0.8
Dehydroabietic acid	9.6	9.2	8.2	8.2	8.5	6.4	6.6	6.5
Oxidised resin acids	1.1	0.6	0.4	0.7	0.8	0.6	0.4	0.2
Neutral compounds	12.5	12	9.8	16.4	15	17.8	21.8	19.8
1-Docosanol	0.4	0.3	0.4	0.1	0.1			
1-Tetracosanol	0.4	0.4	0.5	0.1	0.1			
Neutral diterpenes	1.6	0.9	0.2	1	1.1	0.6	0.9	0.8
Campesterol	1.2	1.1	1.2	0.5	0.4	0.3	0.4	0.4
β -Sitosterol	6	6.3	5.1	5.5	5	5.4	6.2	6.2
β -Sitostanol	0.8	0.9	0.6	1.3	1	1.2	1.6	1.5
Cycloartanol	1.2	1.3	0.5	0.8	1.1	1	1.2	1.1
24-Methylenecycloartanol	0.9	0.8	0.8	1.5	1.1	1.7	1.9	1.7
Lupeol				0.8	0.7	0.7	0.7	0.4
Citrostadienol				1.5	1.1	2	2.5	2.2
Betulinol + methyl betulinate				1.3	1	1.5	2.2	2.2
Squalene				0.5	0.5	1.5	1.6	1.6
Betulaprenols				1.5	1.8	1.9	2.6	1.7

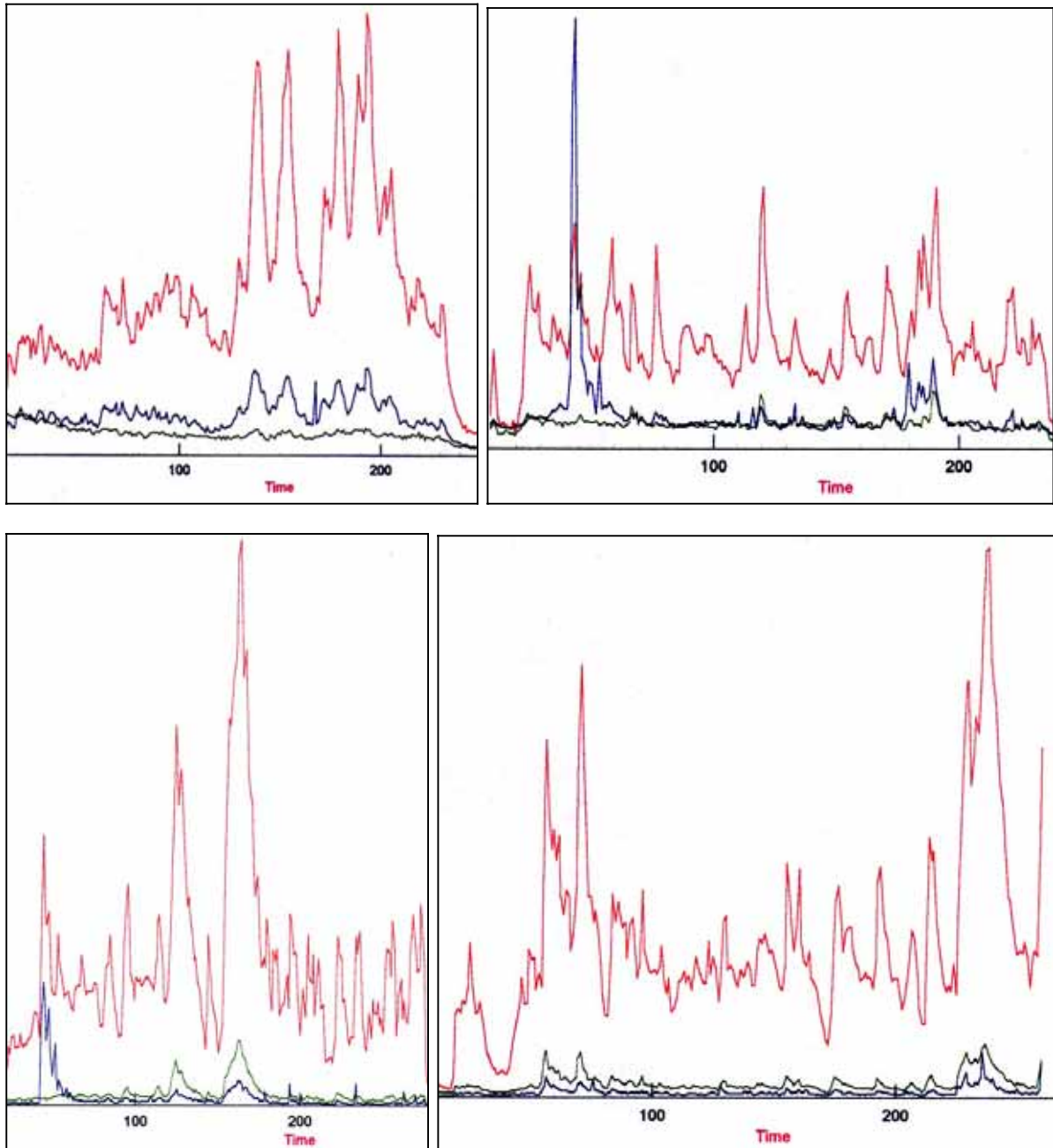
Appendix 4. Examples of non-process elements determination on the frozen surface of selected soap samples (using laser ablation – ICP-MS technique).



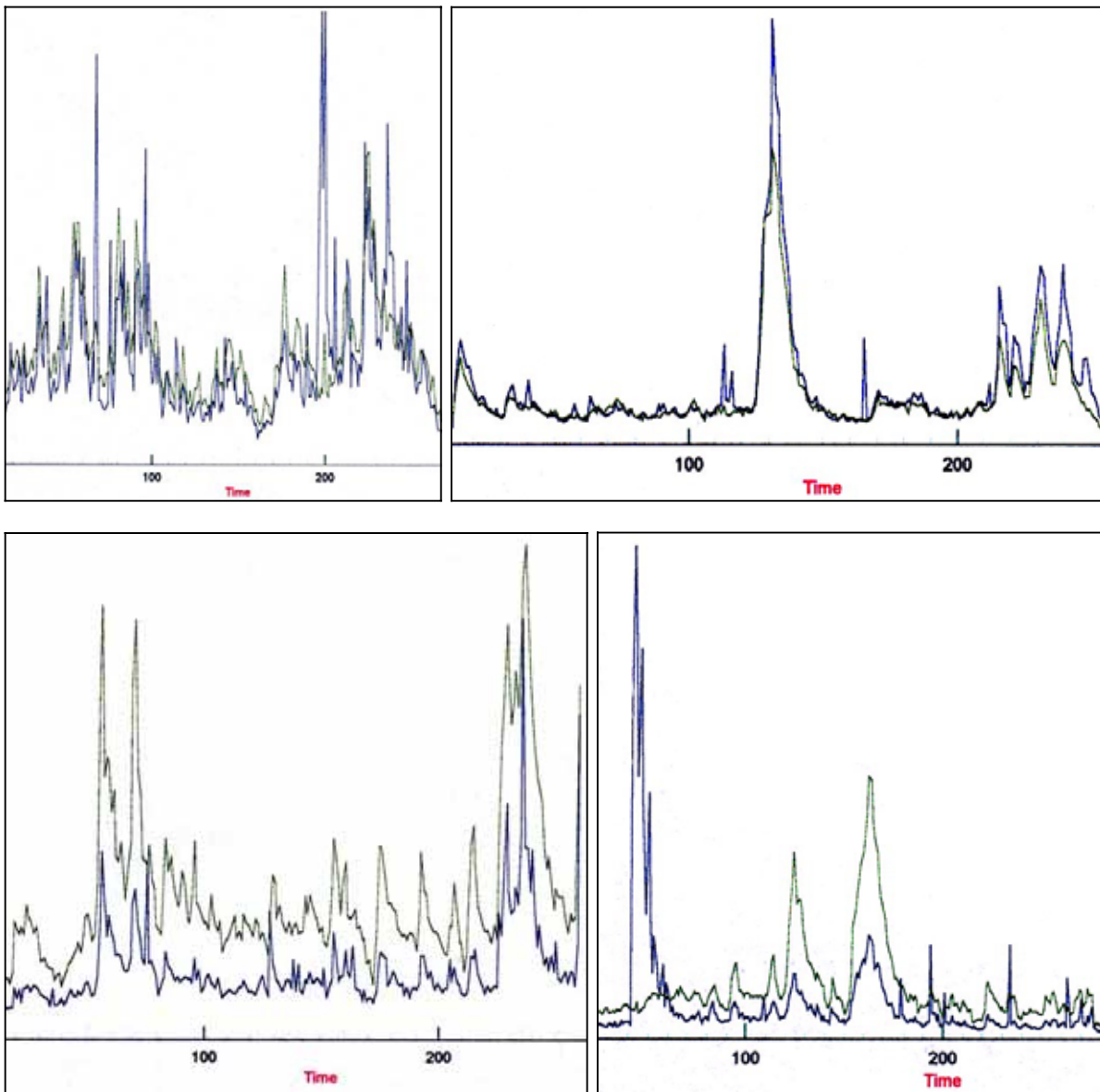
Appendix 4a. Four examples of the distribution of calcium (red), potassium (blue), and manganese (green).



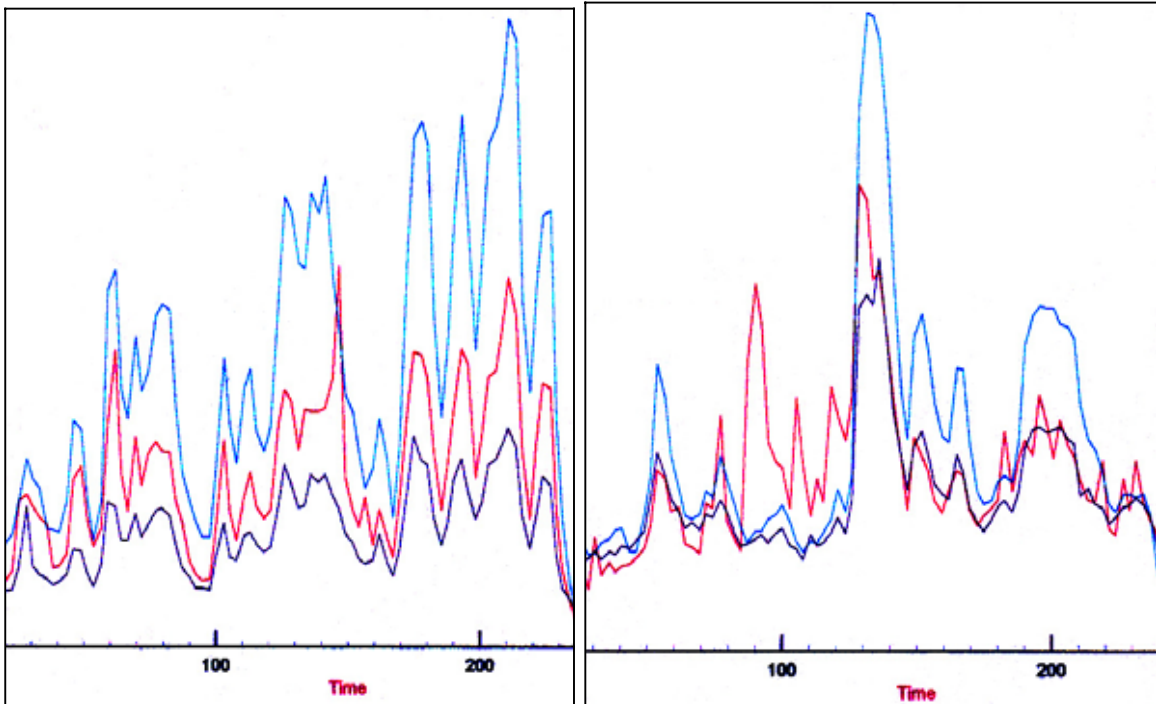
Appendix 4b. Four examples of the distribution of magnesium (red), silicon (green), and aluminum + phosphorus (two bottom lines).



Appendix 4c. Four examples of the distribution of magnesium (red), aluminum (blue), and phosphorus (green).

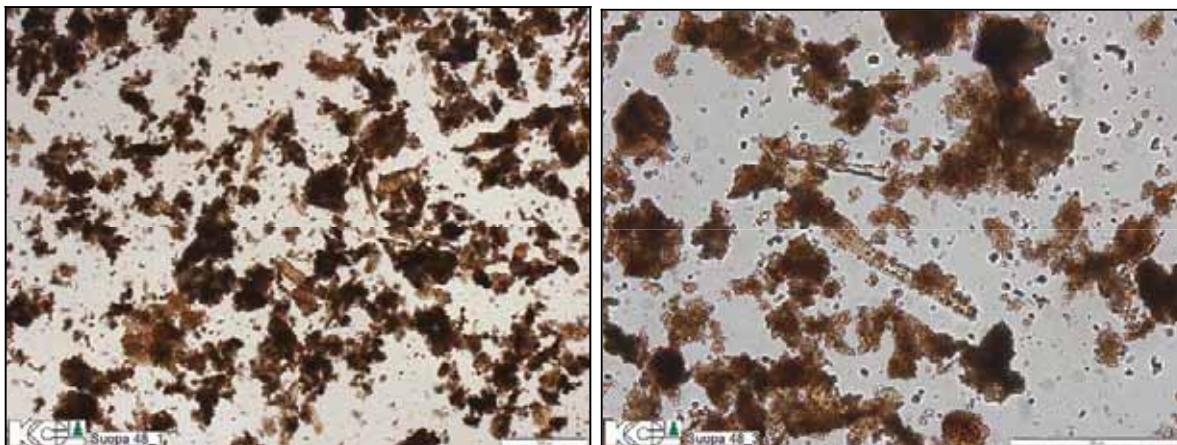


Appendix 4d. Four examples of the distribution of aluminum (blue) and phosphorus (green).

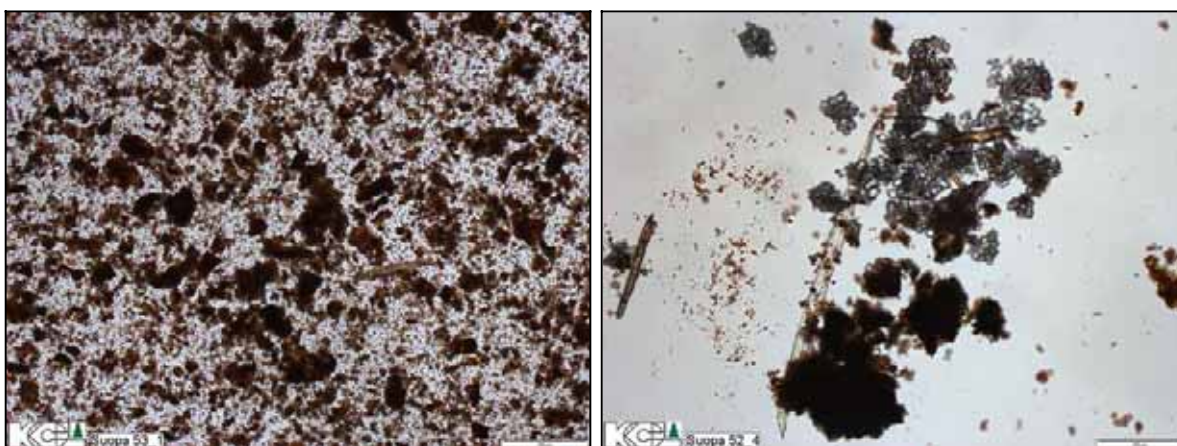


Appendix 4e. Two examples of the distribution of zinc (magenta), aluminum (blue) and phosphorus (red).

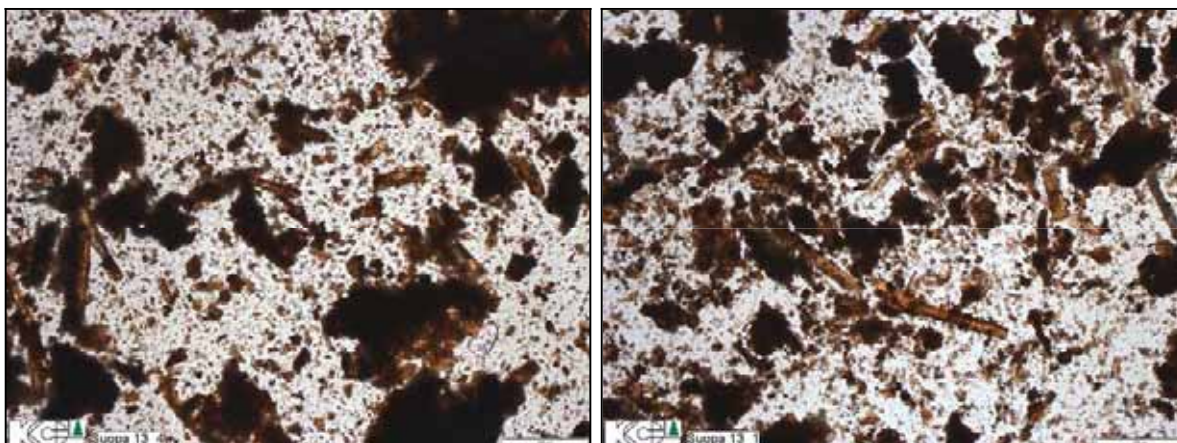
Appendix 5. Photos of fibers and other solid impurities ("dirt") isolated from different soap samples. The acidulations were conducted by sulfuric acid, unless otherwise stated. The scale bar = 200 μ m unless otherwise stated.



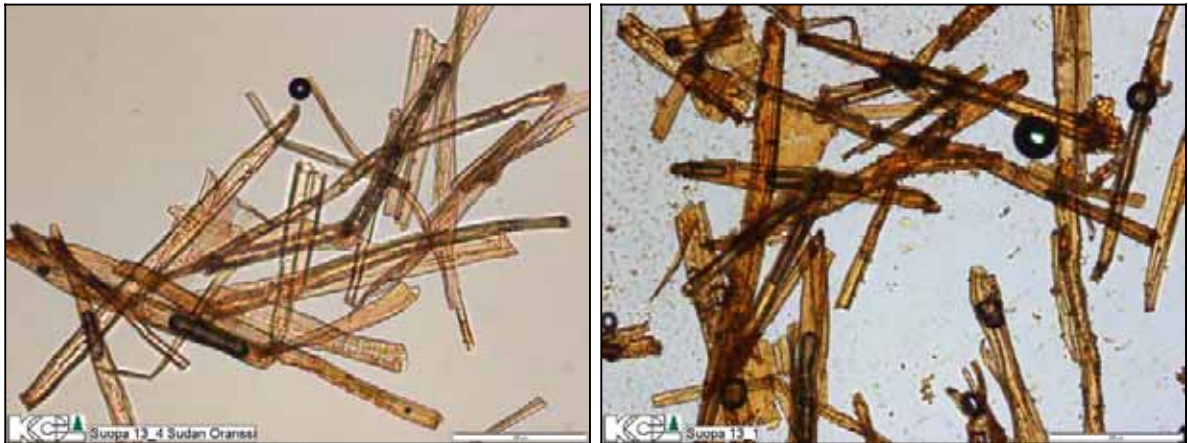
5.1. Joutseno, weak liquor soap.



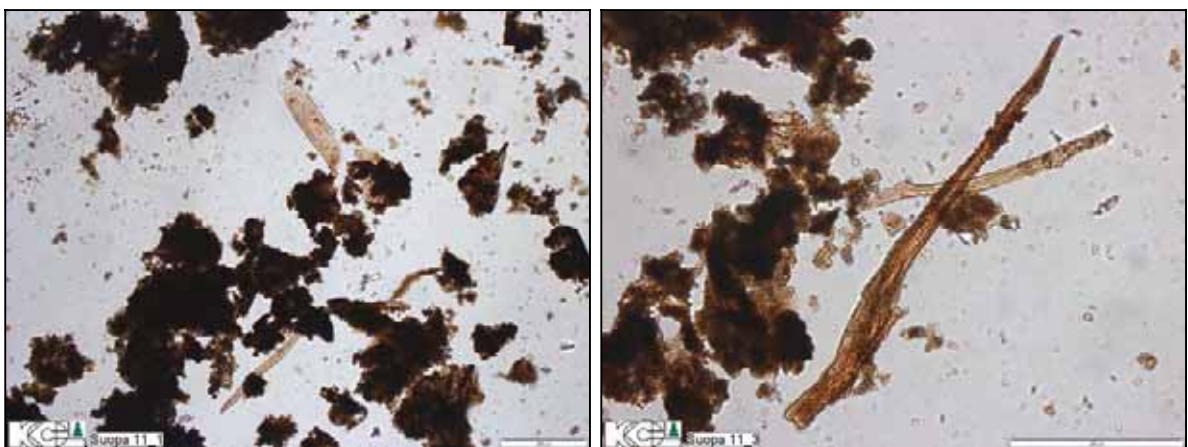
5.2. Kaskinen, intermediate liquor (left) and acidulation feed (right) soaps.



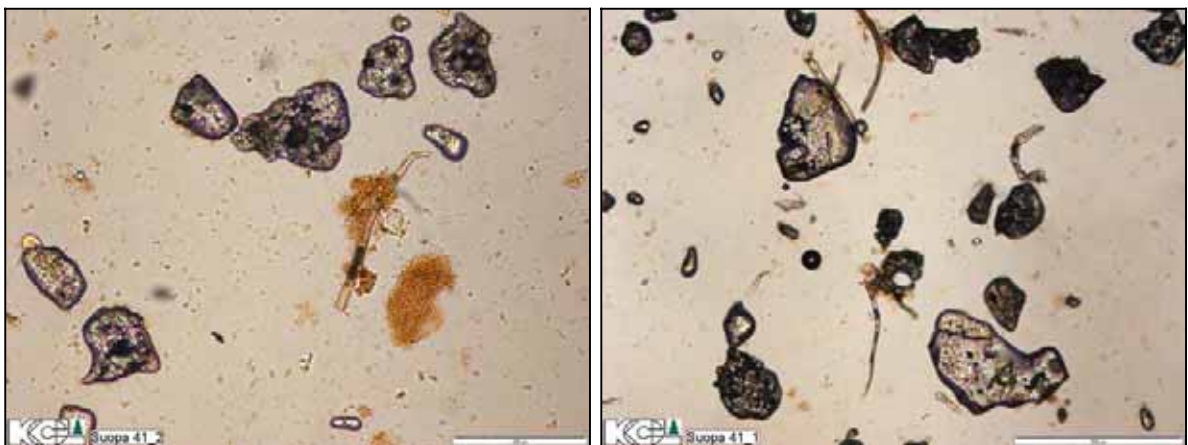
5.3. Kemi, acidulation feed soap.



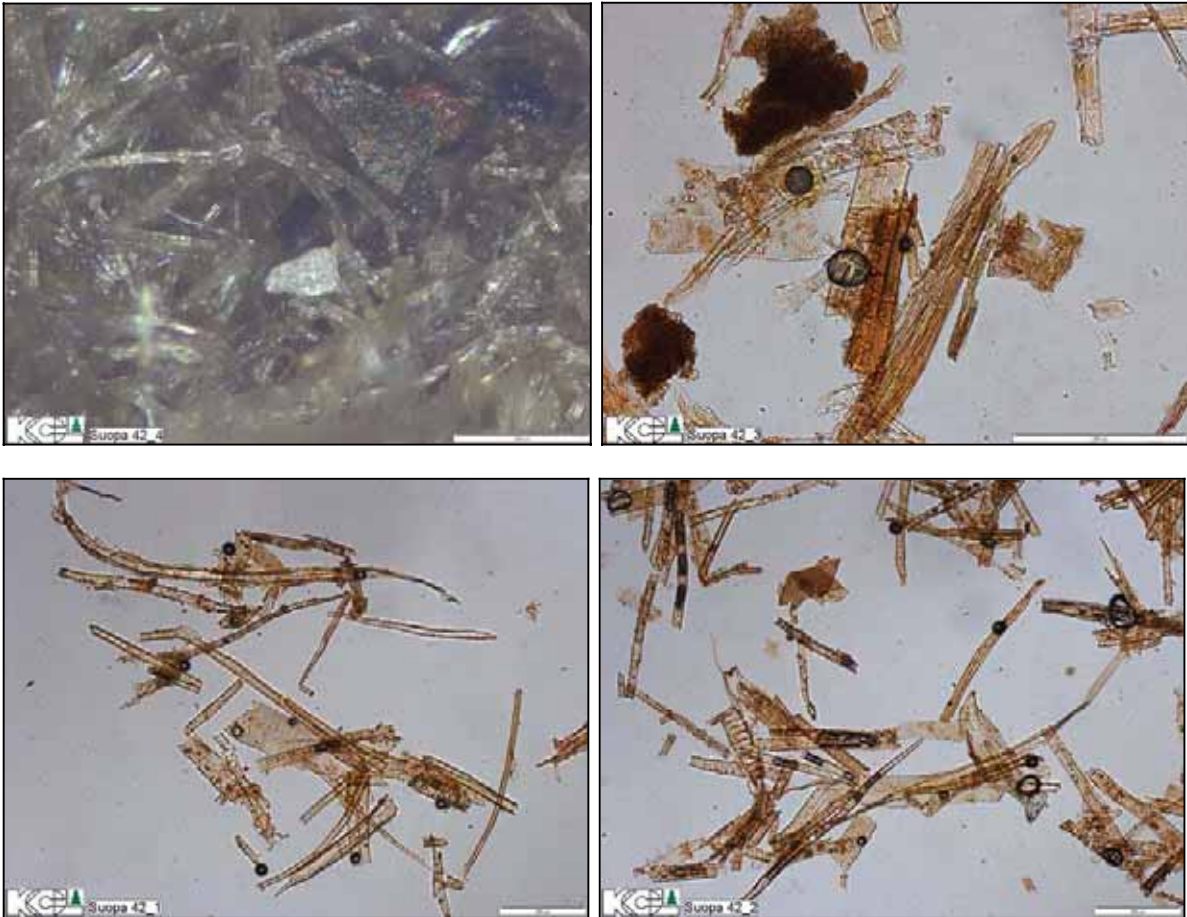
5.4. Kemi, acidulation feed soap (hydrochloric acid acidulation).



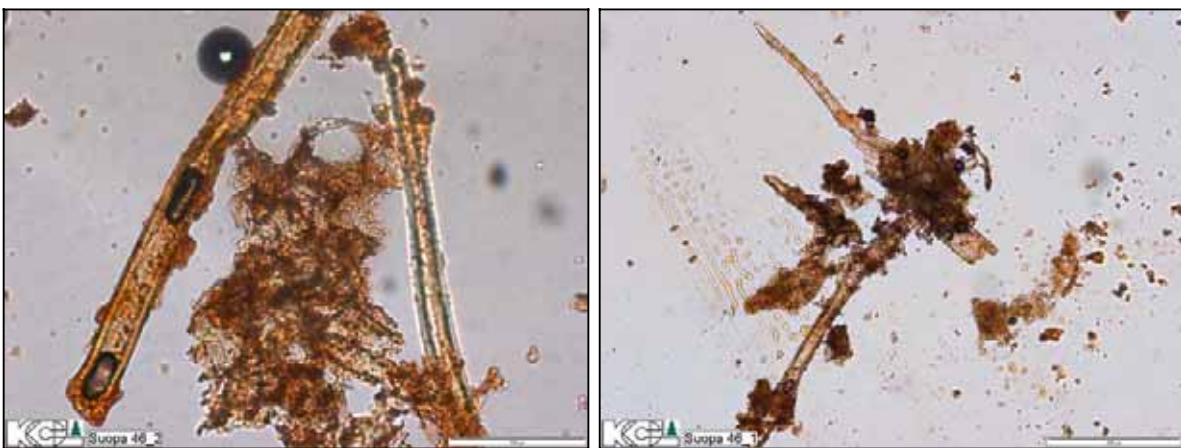
5.5. Rauma, collecting tank soap.



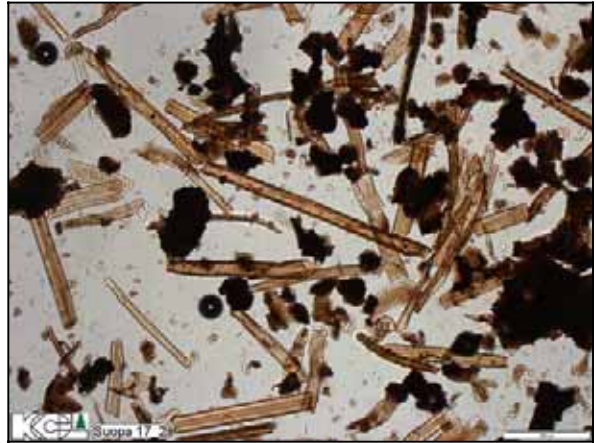
5.6. Äänekoski, acidulation feed soap (hydrochloric acid acidulation). On the right, the scale bar is 500 μm .



5.7. Kaukas, chemical plant soap (filtered mat and its breakdown products).



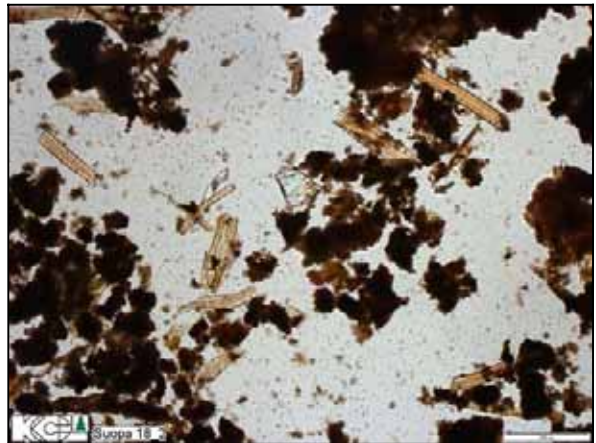
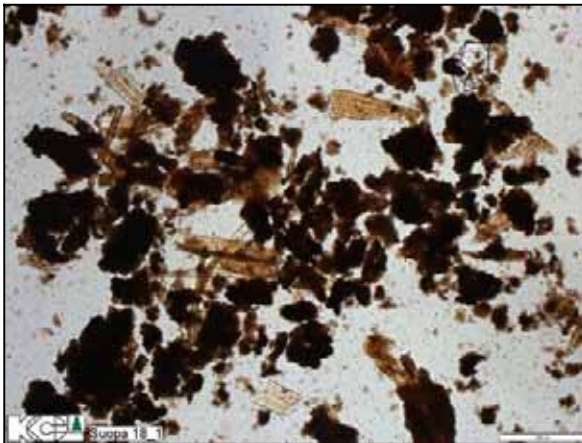
5.8. Kaukas, acidulation feed soap. On the left, the scale bar is 100 μm .



5.9. Kymi, feed liquor 2 soap.



5.10. Kymi, intermediate liquor 1 soap.



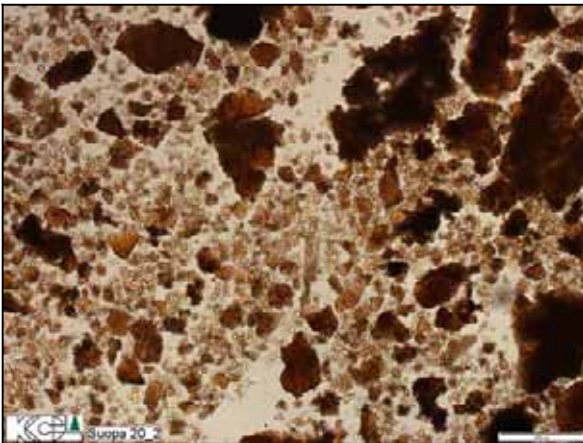
5.11. Kymi, intermediate liquor 2 soap.



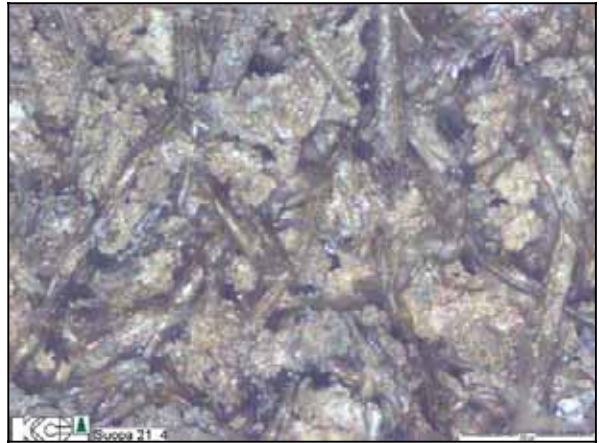
5.12. Kymi, acidulation feed soap (hydrochloric acid acidulation).



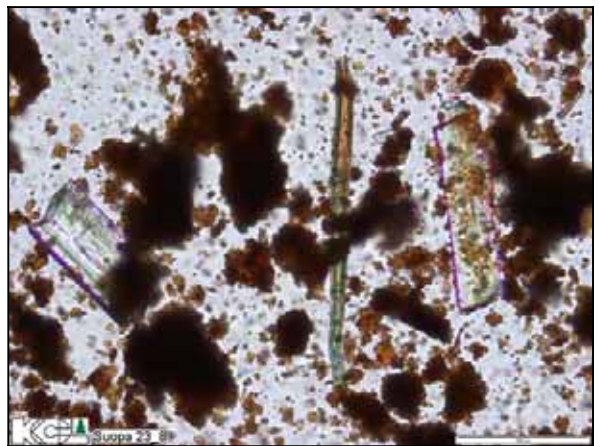
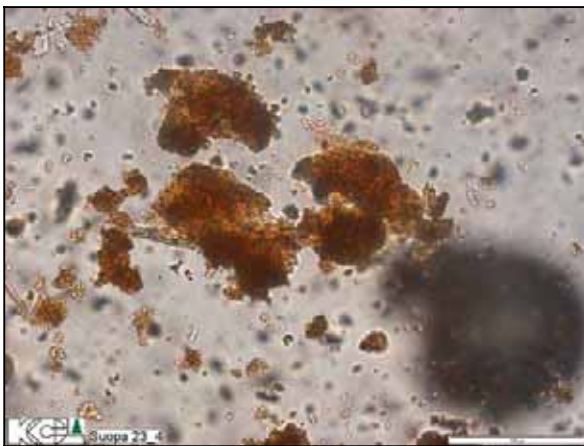
5.13. Pietarsaari, acidulation feed soap.



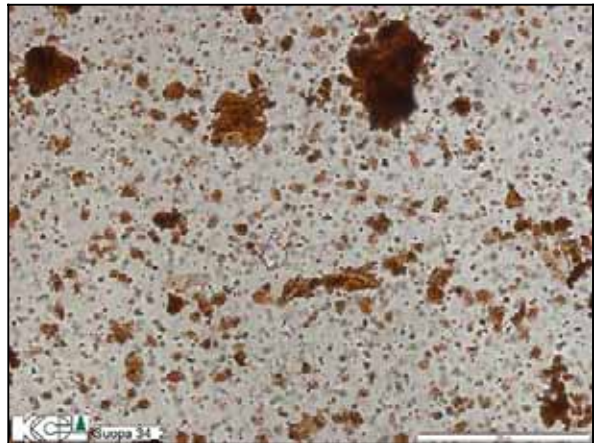
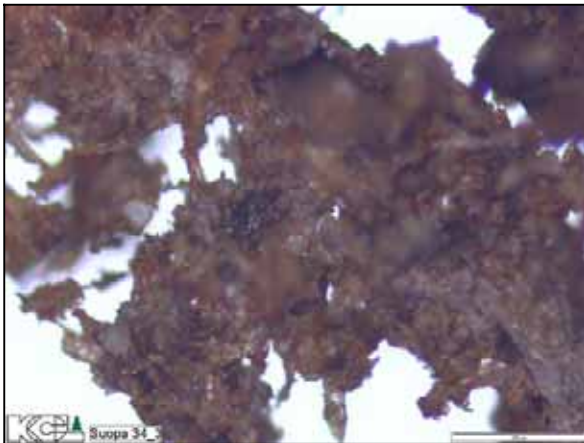
5.14. Tervasaari, SAP soap.



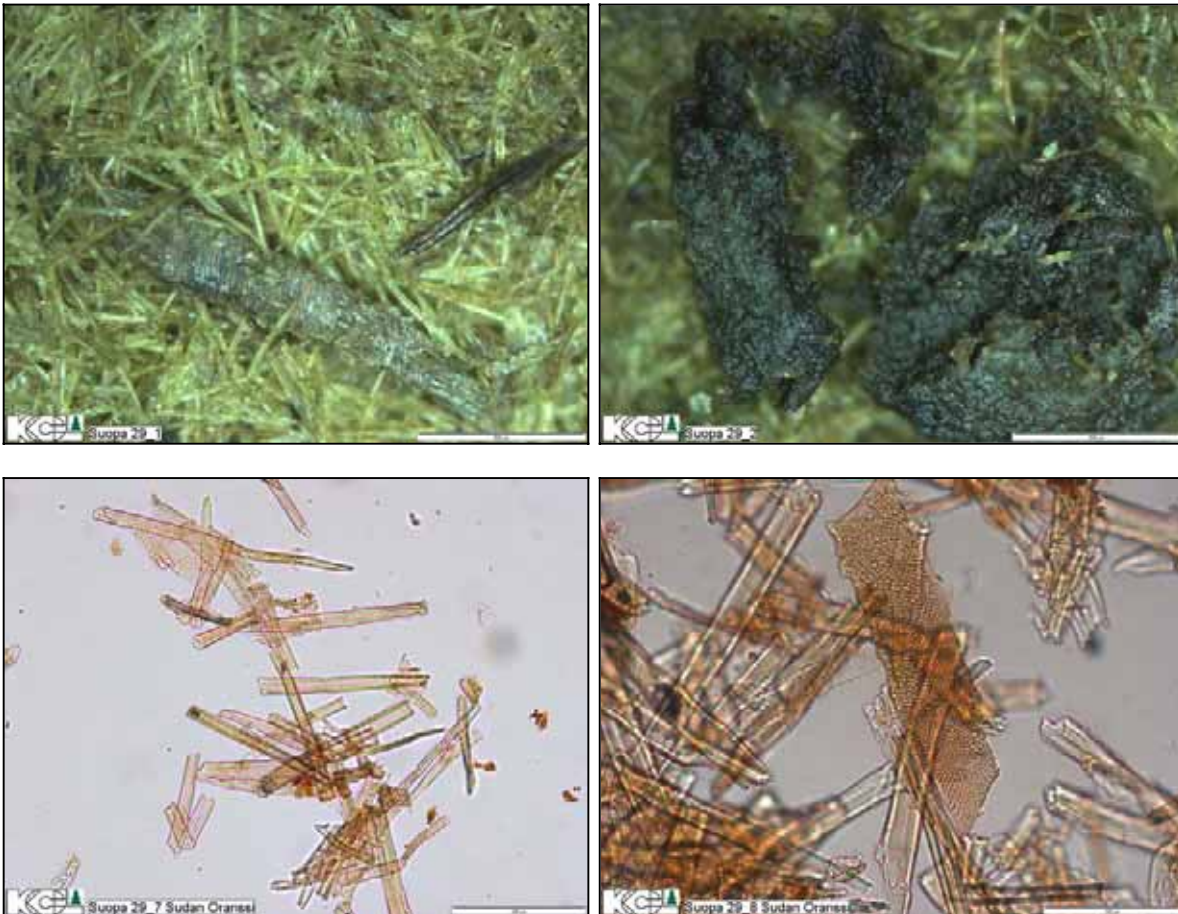
5.15. Tervasaari, kraft weak liquor soap.



5.16. Tervasaari, acidulation feed soap. On the left, the scale bar is 100 μm .



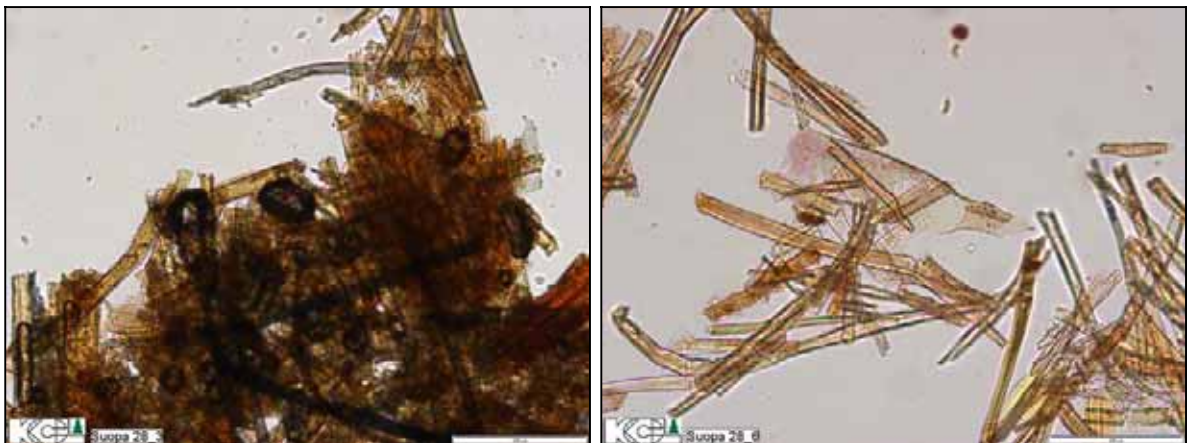
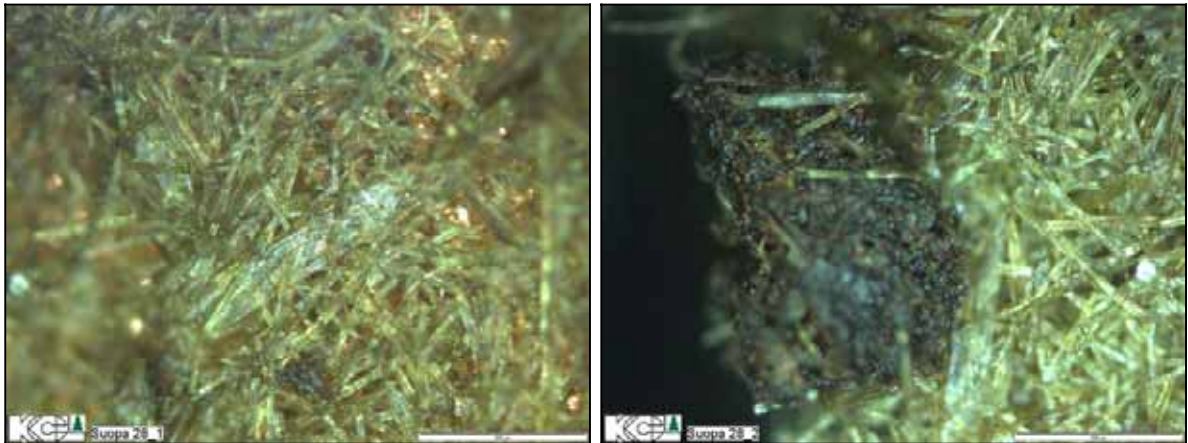
5.17. Sunila, acidulation feed soap.



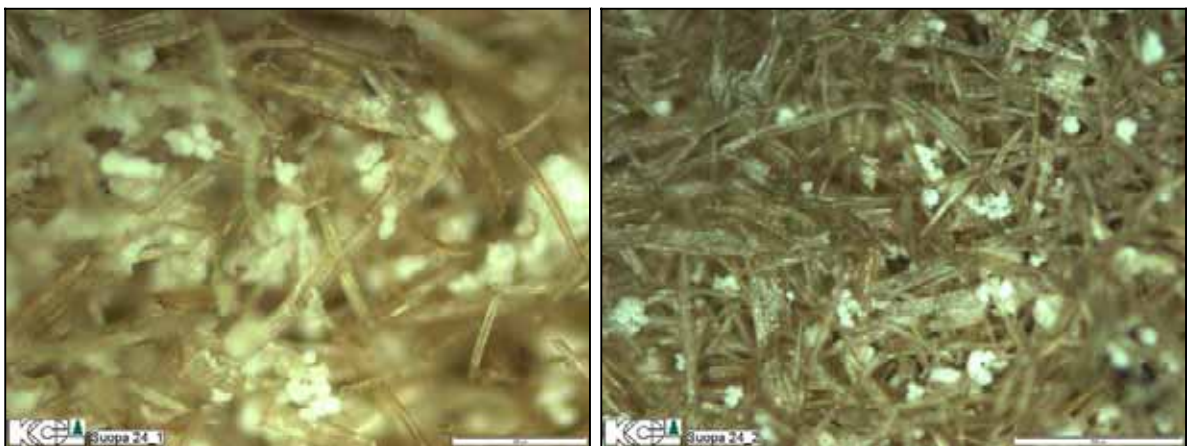
5.18. Enocell, feed liquor 1 soap (filtered mat and breakdown products). The scale bar is 500 μm for the two top photos; on the right (bottom) it is 100 μm .



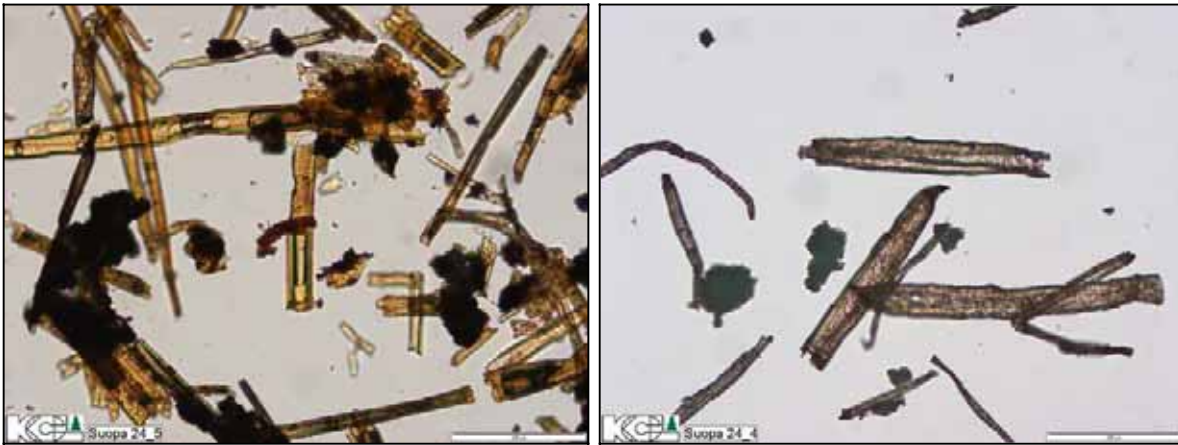
5.19. Enocell, intermediate liquor soap.



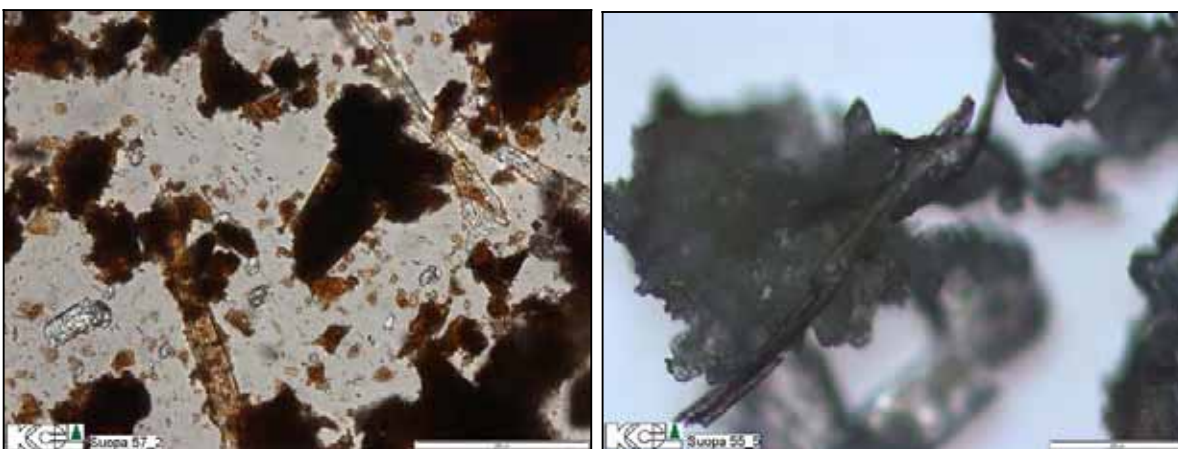
5.20. Enocell, acidulation feed soap. The scale bar is 500 μm for the two top photos.



5.21. Imatra, acidulation feed 2 soap (with white calcium sulfate crystals). The scale bar on the right is 500 μm .



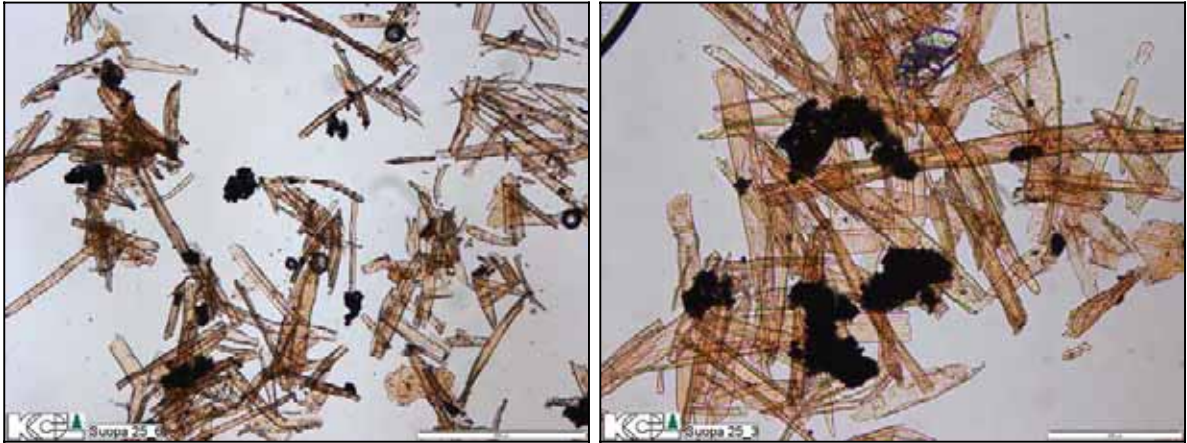
5.22. Imatra, acidulation feed 2 soap.



5.23. Kemijärvi, intermediate liquor soap (left) and acidulation feed soap (right, hydrochloric acid acidulation).



5.24. Kotka, feed liquor (left) and intermediate liquor (right) soaps.



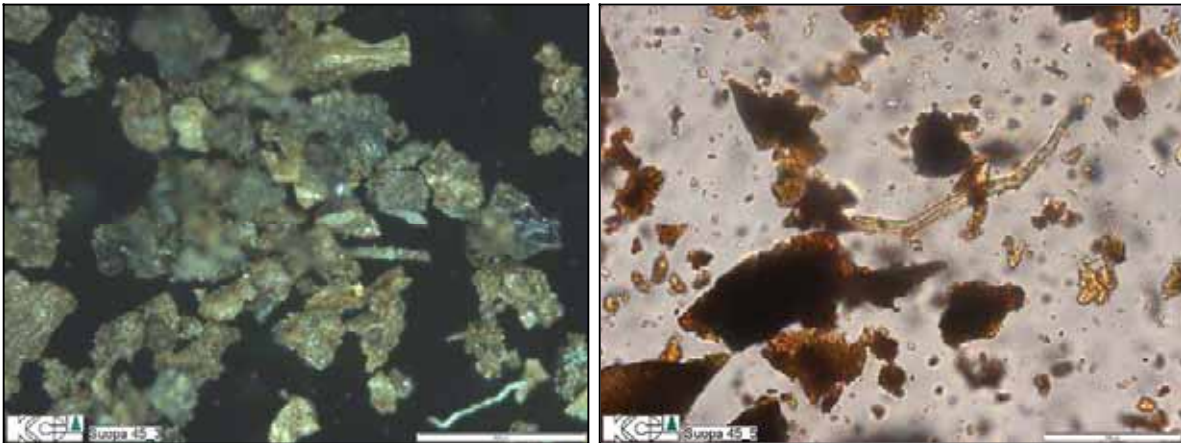
5.25. Kotka, acidulation feed soap (hydrochloric acid acidulation). On the left, the scale bar is 500 µm.



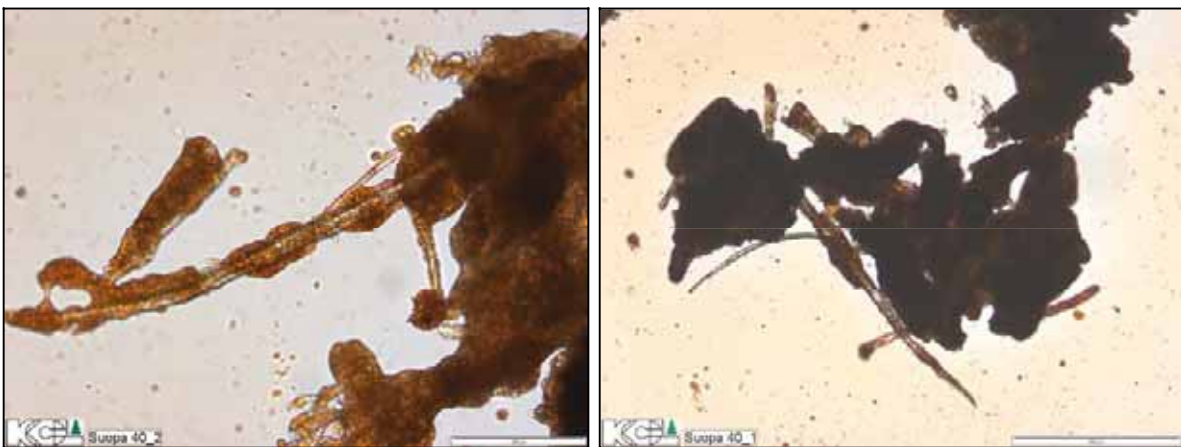
5.26. Oulu, acidulation feed soap. Dark brown spots (right) contain silicone-base material (defoamer). On the left, the scale bar is 100 µm.



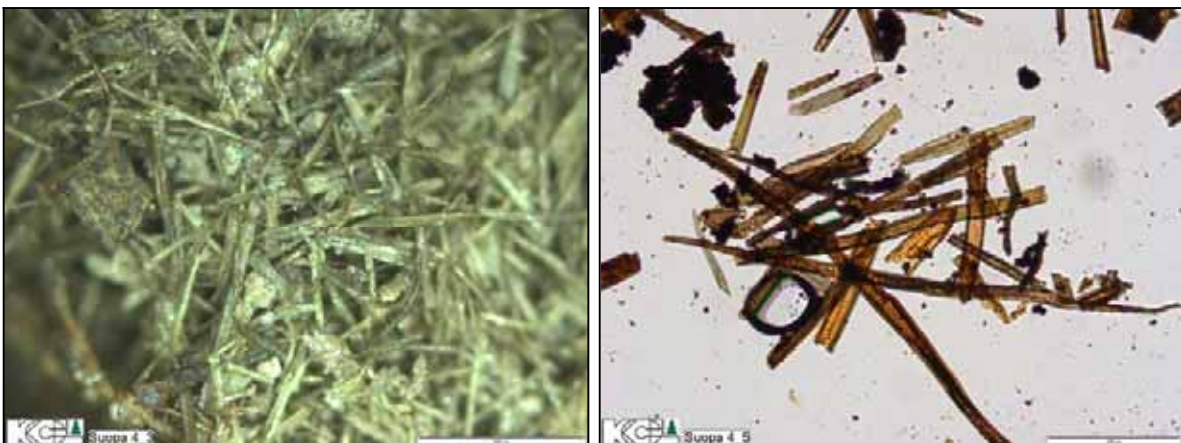
5.27. Varkaus, feed liquor 2 soap. On the left, the scale bar is 500 µm.



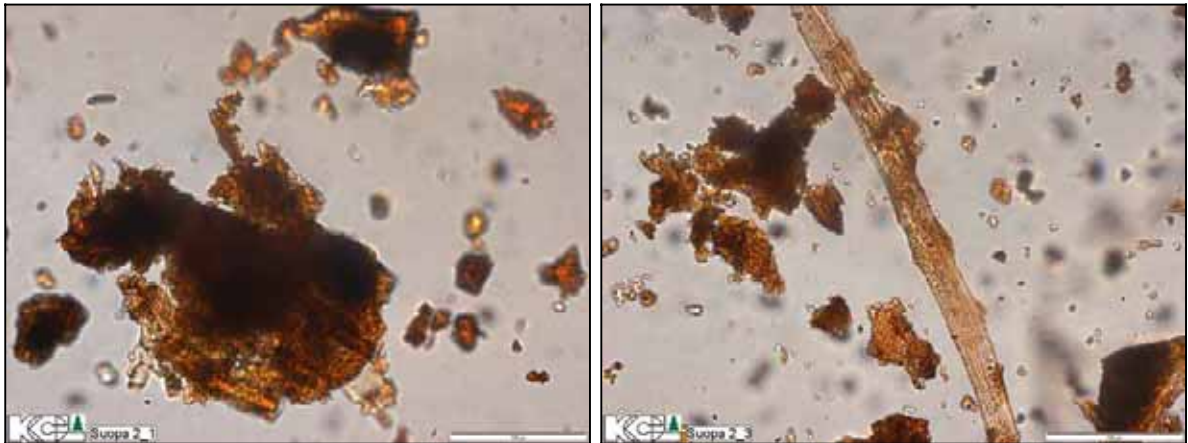
5.28. Varkaus, intermediate liquor soap. The scale bar is 500 μm on the left, and 100 μm on the right.



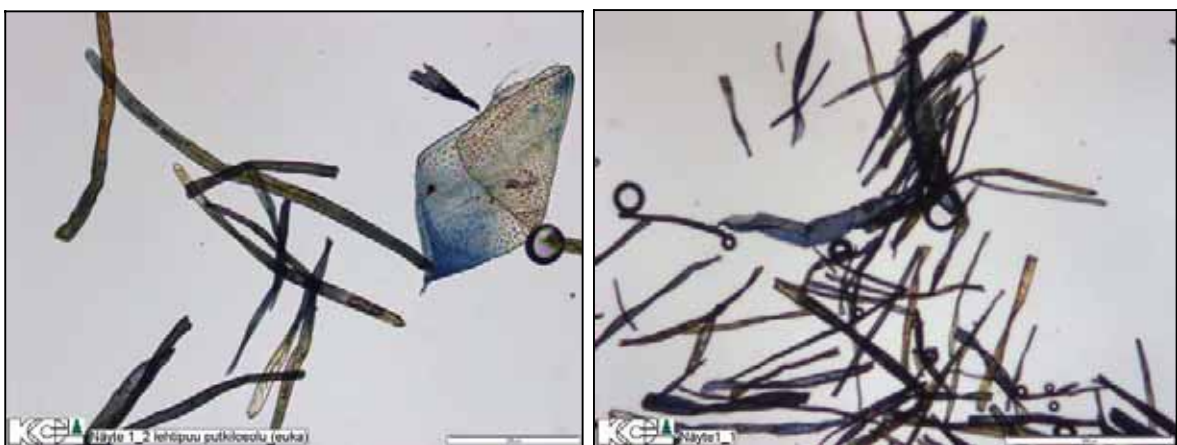
5.29. Varkaus, acidulation feed soap. On the right, the scale bar is 500 μm .



5.30. Veitsiluoto, feed liquor 1 soap. On the left, the scale bar is 500 μm .



5.31. Veitsiluoto, intermediate liquor 1 soap. The scale bar is 100 μm .



5.32. Veitsiluoto, acidulation feed soap. On the right, the scale bar is 500 μm .

APPENDIX 6 – SELECTED MILL DATA

This appendix summarises the main results of the mill survey (2004), based on the answers received after sending the questionnaire. In many cases, a number of unnecessary details were removed from the replies, just to decrease the risk of accidentally releasing confidential process information. The short descriptions given below have also been checked by the corresponding mill staff.

Botnia, Joutseno

Pulping process: Compact cooking, 100% softwood.

Fiber line additives: Silicone-based defoamer.

Soap separation and handling: Soap separation rate is approximately 80 kg per ton of pulp, of which 50–60% from the wash and feed liquor tanks, and 40–50% from the intermediate liquor tank. The weak and feed liquor tanks (equipped with the soap spouts) are skimmed in turn; the intermediate liquor tank is always kept full and the soap decanted. Some black liquor is removed from the soap in the collection tank, after which the soap is taken for further liquor removal to the storage tank 1. From this tank the soap is taken to the storage tank 2 by decanting. Feed to the acidulation is from the storage tank 2.

Soap acidulation: Two-stage acidulation with CO_2 and H_2SO_4 , the corresponding consumptions being c. 70–80 and 200–400 kg per ton of tall oil. The tall oil yield varies from 50 to 70%, depending on soap quality. Typical tall oil production is 35 kg/t pulp.

Further information: Diploma thesis by Viitala (2005) describes soap acidulation tests in the presence of lignosulfonates.

Botnia, Kaskinen

Pulping process: Continuous cooking, 100% hardwood (mainly birch, some short-period aspen campaigns). Also sawdust cooking (Bauer).

Fiber line additives: Silicone-based defoamer, and rosin soap during cooking.

Soap separation and handling: Soap separation rate is approximately 26 kg per ton of pulp (average in 2003), of which c. 60% from the feed liquor tanks, and 40% from the intermediate liquor tank. The soap skimmed in the liquor tanks is led for liquor removal into the washing tank, from which it is taken by decanting to the acidulation feed tank.

Soap acidulation: The acidulation chemical is the spent (waste) acid from the chlorine dioxide plant (HPA).

Botnia, Kemi

Pulping process: Continuous cooking (2 digesters), 70% softwood (mainly pine) and 30% birch. Also sawdust cooking.

Fiber line additives: Oil- and silicone-based defoamers.

Soap separation and handling: Soap separation rate is approximately 125 kg per ton of pulp, of which c. 98% from the feed liquor tanks, and 2% from the intermediate liquor tank. The feed liquor tank 1 is skimmed continuously, and the feed liquor tank 2 approximately every two days. The liquor removal from the soap takes place in two consecutive storage tanks, before acidulation.

Soap acidulation: Two-stage acidulation process with CO_2 and H_2SO_4 is in the use. The tall oil yield is 40–50%, depending on the soap quality. The average production rate is 60 kg/t of pulp.

Further information: The first two-stage acidulation process in Finland has been described by Rouvinen (1993) and Koljonen and Kivilinna (1995). Nikka (2000) has previously determined soap balance at this mill.

Botnia, Rauma

Pulping process: SuperBatch cooking, 100% softwood.

Fiber line additives: Silicone-based defoamer.

Soap separation and handling: The soap separation rate is approximately 46–50 kg per ton of pulp, and is totally removed (to the collection tank) in the two feed liquor tanks. From the collection tank the soap is pumped into two storage tanks which feed the acidulation system in turn.

Soap acidulation: Two-stage acidulation with CO_2 and H_2SO_4 , the corresponding consumptions being c. 130 and 280 kg per ton of tall oil. The tall oil yield is c. 40%, making 46–50 kg/t pulp.

Botnia, Äänekoski

Pulping process: Continuous cooking, both softwood and hardwood.

Fiber line additives: Silicone-based defoamer.

Soap separation and handling: The soap is separated in the feed liquor (50%) and intermediate liquor (50%) tanks. The separated soap is taken to the collection tank for some liquor removal, from which it is taken to two storage tanks (where more liquor is removed). They feed the acidulation reactor in turn.

Soap acidulation: The soap is acidulated with H_2SO_4 , typical consumption is 215 kg/t of tall oil.

UPM, Kaukas

Pulping process: SuperBatch cooking, both softwood and birch.

Fiber line additives: Silicone-based defoamers.

Soap separation and handling: The soap is separated in the feed liquor (80%) and intermediate liquor (20%) tanks. The removal of black liquor from the soap takes place in two storage tanks and in the feed tank. Part of the soap is extracted (2004) for the recovery of neutral compounds before acidulation.

Soap acidulation: The soap is acidulated with H_2SO_4 , typical consumption is 245 kg/t of tall oil. The yield of tall oil is c. 80%, making 29 kg/t pulp.

UPM, Kymi

Pulping process: Continuous cooking (2 digesters), birch 61% and pine 39%.

Fiber line additives: Silicone-based defoamer (pine fiber line) and a deresination chemical (birch fiber line).

Soap separation and handling: The soap is separated in the feed liquor (80%) and intermediate liquor (20%) tanks, at the evaporator trains 1 (birch) and 2 (mixed birch/pine). The feed liquor tanks are skimmed 2–4 times per week, and the intermediate liquor tanks 1–2 times per week. The skimmed soaps are delivered to the soap (feed) tank.

Soap acidulation: The acidulation chemical is H_2SO_4 . The consumption was c. 215 kg/t of tall/birch oil in 2003.

UPM, Pietarsaari

Pulping process: Continuous and SuperBatch cooking, both softwood and hardwood.

Fiber line additives: Silicone-based defoamers at each fiber line.

Soap separation and handling: The soap is separated (by decantation) mainly from the feed liquor tanks, only a little from the intermediate liquor tank. Black liquor is removed from the soap in the collection tank and two storage tanks, before pumping to the acidulation feed tank.

Soap acidulation: Two-stage acidulation process with CO_2 and H_2SO_4 is in the use, but the typical consumption figures have not yet (2004) been established. The tall oil yield is 20–35%, making the production rate 20–50 kg/t pulp.

UPM, Tervasaari

Pulping process: Kraft and SAP batch cooking, 100% softwood. Also sawdust cooking.

Fiber line additives: Silicone-based defoamers.

Soap separation and handling: Altogether, some 80 kg of soap per ton of pulp is recovered, of which 70% from kraft weak liquor tanks, 10% from kraft intermediate liquor tank, and 20% from the SAP weak and intermediate liquor tanks. All the soaps are collected in the same storage tank for liquor removal.

Soap acidulation: The soap is acidulated at other mills (or burnt in the recovery boiler).

Sunila

Pulping process: Compact cooking, 100% softwood (60% pine, 40% spruce).

Fiber line additives: Silicone-based defoamer.

Soap separation and handling: Approximately 75% of the recovered soap is skimmed in three feed liquor tanks, and 25% in two intermediate liquor tanks (one tank per evaporator train). There are separate collection tanks for the feed and intermediate liquor soaps. After some liquor removal, both of these tanks feed soap handling tank 1 for the more efficient liquor removal. From this, the soap is delivered to the 2nd soap handling tank for further liquor removal, after which the soap is taken to the tall oil acidulation plant. This plant has four small tanks of which three are used for the final liquor removal, and one feeds the acidulation reactor.

Soap acidulation: The acidulation chemical is the spent (waste) acid from the chlorine dioxide plant (HPA). The yield of tall oil is 45–50%, making 40–50 kg/t of pulp.

Further information: Passinen (1998) has previously determined the soap balance at this mill.

Stora Enso, Enocell

Pulping process: SuperBatch cooking, 65% birch and 35% softwood (mainly pine).

Fiber line additives: Silicone-based defoamer.

Soap separation and handling: Approximately 95% of soap is recovered (by decanting) in the feed liquor tanks, and some 5% in the intermediate liquor tank. After some liquor removal in the storage tank (with cooling), the soap is taken to the acidulation feed tank.

Soap acidulation: The acidulation is carried out with H_2SO_4 . The yield of tall oil is 40–50%. The production rates are not fully known as a significant part of the soap is burnt in the recovery boiler.

Stora Enso, Imatra

Pulping process: Batch cooking (100% softwood) at Tainionkoski; continuous cooking (2 digesters) at Kaukopää, c. 70% birch and 30% softwood.

Fiber line additives: Oil-based defoamers are used at all three fiber lines.

Soap separation and handling: Soap is separated at the wash, feed, and intermediate liquor tanks of two liquor lines (although the share is not exactly known). The softwood and birch liquors are mixed between the wash and feed liquor tanks. The soap separation is increased (2004) by injecting air into the softwood liquor at the wash liquor line, into all the feed liquor tanks, and into the liquor lines running into the intermediate liquor tanks. The separated soap is subjected to liquor removal in two storage tanks (one tank per evaporator train), before pumping into the two soap tanks. These tanks are equipped with partition walls for further liquor removal, before feeding to the acidulation reactor.

Soap acidulation: The acidulation is carried out with H_2SO_4 ; the consumption is c. 270 kg per ton of tall oil.

Stora Enso, Kemijärvi

Pulping process: SuperBatch cooking, 100% softwood (mainly pine).

Fiber line additives: Silicone-based defoamers.

Soap separation and handling: Soap is separated by decantation at the wash liquor (70% of the total soap), feed liquor (27%), and intermediate liquor (3%) tanks. Some liquor is removed from the separated soap in the soap tank 1, after which the soap is led to the soap washing/storage tank 2. There are two soap tanks (2A and 2B), used in turn as a soap washing or storage tank. The washing liquor is typically neutralized spent acid from tall oil acidulation. The washed soap is pumped to the feed tank where further soap washing is also possible, if needed.

Soap acidulation: The acidulation is conducted mainly with the waste acid from the chlorine dioxide plant (Mathieson). Only occasionally, some sulfuric acid is also used.

Further information: Passinen (1998) has determined soap balance at this mill.

Stora Enso, Kotka

Pulping process: Sawdust cooking (Bauer).

Fiber line additives: Silicone-based defoamer. Anthraquinone and carbon dioxide are also used.

Soap separation and handling: Soap is separated by decantation from the wash liquor, feed liquor, and intermediate liquor tanks. The share is approximately one third in each area.

Soap acidulation: There is no soap acidulation at this mill.

Stora Enso, Oulu

Pulping process: Continuous cooking, c. 40% birch and 60% softwood (mainly pine).

Fiber line additives: Silicone-based defoamer.

Soap separation and handling: Soap separation rate is approximately 170 kg per ton of pulp, of which c. 75% is from the feed liquor tanks and 25% from the intermediate liquor tanks. Liquor is removed from the isolated soap in the collection, wash, and storage tanks before pumping to the acidulation feed tank.

Soap acidulation: For the soap acidulation, mainly spent (waste) acids from the chlorine dioxide plants (of other pulp mills) are used. In addition, some sulfuric acid is also used. The yield of tall oil is c. 85 kg/t of softwood pulp.

Stora Enso, Varkaus

Pulping process: Continuous cooking, both birch and softwood.

Soap separation and handling: Soap is skimmed at the weak liquor tanks (twice a week) and the intermediate liquor tank (every two days), with the share of 70% from the weak liquor tanks. The soap is led to the soap collection tank for the liquor removal. The soap is then pumped to the storage tank 1 for further liquor removal. The soap flow continues to the storage tank 2 which is a so-called double tank; soap rises over the partition wall to the 3rd tank which feeds the acidulation reactor.

Soap acidulation: The soap is acidulated with the waste acid from the chlorine dioxide plant (Mathieson). The yield of tall oil is c. 50%.

Stora Enso, Veitsiluoto

Pulping process: Continuous cooking, hardwood 60% (mainly birch) and softwood 40% (mainly pine).

Fiber line additives: Silicone-based defoamer.

Soap separation and handling: Total soap recovery rate is approximately 66 kg/ton of pulp. Of this, 5% is isolated from the wash liquor tank, 80% from the feed liquor tank, and 15% from the intermediate liquor tank.

Soap acidulation: The soap is acidulated with the waste acid from the chlorine dioxide plant (HPA). The yield of tall oil is c. 34 kg/ton of pulp.

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